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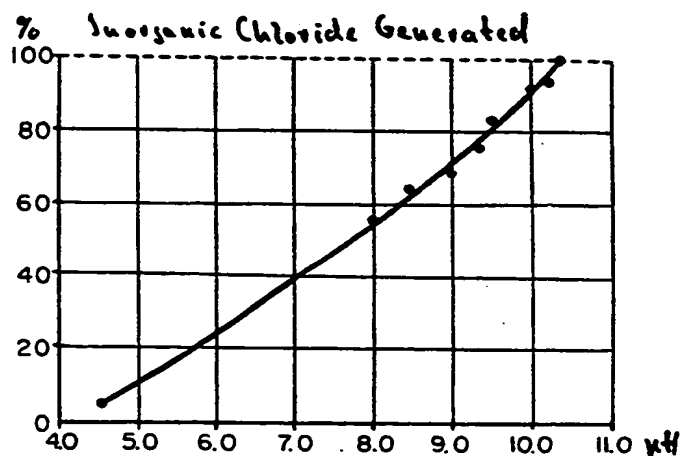
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(54) **Phosphorus containing surface active agents and their preparation.**

(57) New phosphate-ester reactants are reacted with an amine reactant which may be primary, secondary or tertiary amine to produce phosphobetain compounds, which compounds exhibit outstanding foaming, viscosity-building, wetting, cleansing, detergency, anti-static and emulsifying properties and are extremely well tolerated by human tissue.



**EP 0013713 A1**

The present invention relates to a novel process for the preparation of phosphorus-containing amphoteric quaternary and zwitterionic surface active agents, and to certain novel surface active agents per se.

### Background of the Invention

Quaternaries, betaines and certain substituted betaines are known in the art but the specific compounds made in accordance with the process of the instant invention have been found to be particularly useful. Thus, the compounds made by the present invention exhibit outstanding foaming, viscosity-building, wetting, cleansing, detergency, anti-static and emulsifying properties and are therefore useful in industrial applications calling for high performance surface active agents. The compounds are also highly stable species and are extremely well tolerated by human tissue, i.e., they exhibit exceptionally low ocular irritation and oral toxicity, and are therefore eminently suited and useful as surface active agents in personal care compositions.

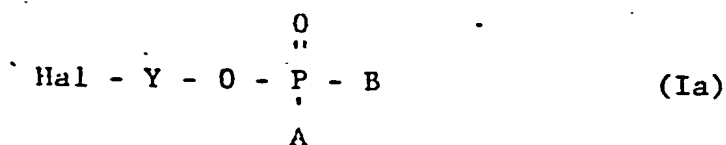
### The Invention

Essentially, the process of the invention comprises reacting a phosphorus-containing reactant, more specifically a phosphate-ester reactant, with an amine reactant, which may be a primary, secondary, or tertiary amine, to produce certain phosphobetain compounds. In additional aspect, the invention

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provides certain novel phosphate ester reactants employed in said process and a process for making such phosphate ester reactants in a manner which makes such reactants eminently suitable for conversion into highly efficacious surface active agents.

The phosphate ester reactants utilized in the invention can be represented by the formula



wherein

Hal is halogen

A is selected from OM, and OY Hal.

B is selected from H, OM', and OYHal.

with the proviso that M' is an organic radical

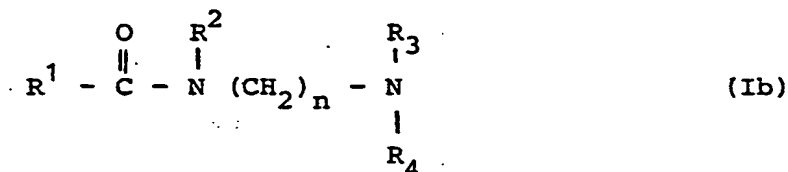
Y may be alkylene, optionally interrupted by up to 3 oxygen atoms, of up to 12 carbon atoms, which alkylene chain may optionally be substituted with lower alkyl, alkoxy, hydroxy or hydroxyalkyl, e.g., of not more than 10 carbon atoms each;

M and M' are individually selected from the following: (a) hydrogen, (b) an organic radical selected from alkyl or hydroxyalkyl of up to 6 carbon atoms, polyhydroxyalkyl of up to 10 carbon atoms, glyceryl, cycloalkyl of up to 6 carbon atoms, aryl or arylalkyl of up to 10 carbon atoms, or (c) a salt radical selected from alkali metals (e.g., sodium or potassium), alkaline earth metals (e.g., magnesium or calcium), and mono-, di-, or triethanolamine.

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The amine reactant can be a primary, secondary, or a tertiary amine. Thus, the amine reactants can carry one, two, or three organic radicals, i. e., they can be primary amines having two hydrogens (hereinafter designated R'), secondary amines (hereinafter R'), or tertiary amines (hereinafter R). Preferably, the amine reactant contains not less than 6 or more than 60 carbon atoms total.

The amines employed in the invention contain from one to three organic radicals, i. e., they may contain optionally substituted alkyl, alkenyl, and alkynyl groups, optionally interrupted by hetero atoms, such as oxygen, nitrogen, or sulfur, and can contain other functional groups, e. g., ester or amido moieties, and the amine substituents may, in the case of the secondary and tertiary amines, be themselves linked together to form N-heterocyclic structure, e. g., morpholino. In preferred and more specific embodiments of the invention, the amine reactant is an amidoamine reactant of the formula



wherein

R<sup>1</sup> is alkyl, alkenyl, alkoxy, or hydroxyalkyl of from 5 to 22 carbon atoms each, or aryl or alkaryl of up to 20 carbon atoms.

R<sup>2</sup> is hydrogen or alkyl, hydroxyalkyl or alkenyl of up to 6 carbon atoms each or cycloalkyl of up to 6 carbon atoms, preferably of from 2 to 5 carbon atoms, or polyoxyalkylene of up to 10 carbon atoms.

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$R^3$  and  $R^4$ , which may be the same or different, are, in the case of the tertiary amines (R), selected from alkyl, hydroxyalkyl, carboxyalkyl of up to 6 carbon atoms in each alkyl moiety, and polyoxyalkylene of up to 10 carbon atoms; in addition,  $R^3$  and  $R^4$ , taken together with the nitrogen to which they are attached, may represent an N-heterocycle, e.g., a morpholino structure, in which the Y radical is bonded to a ring atom of said N-heterocycle other than the nitrogen of the R moiety; in the case of the secondary amines ( $R'$ ), one of  $R^3$  and  $R^4$  is hydrogen, and in the case of the primary amines ( $R''$ ), both  $R^3$  and  $R^4$  are hydrogen;

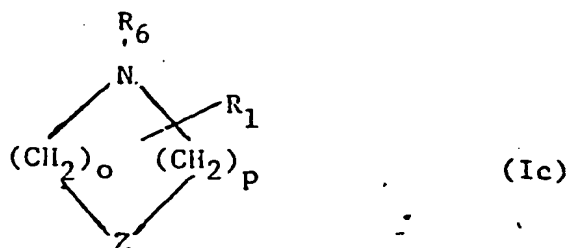
n is an integer from 2 to 12.

(The term "polyoxyalkylene radical" as used above in the definition of  $R^2$ ,  $R^3$  and  $R^4$  may be of the formula  $(R^5 - O - R^{5'})_m$  wherein  $R^5$  and  $R^{5'}$  are alkyl of from 1 to 4 carbon atoms and m is an integer from about 2 to 10).

In different specific and preferred embodiment, the secondary ( $R'$ ) and tertiary (R) amine reactants of the invention may be an N-heterocyclic radical which may contain one additional hetero atom (e.g., oxygen or another nitrogen) and contains 5 to 6 total ring carbon atoms; optionally, said heterocyclic radical may be substituted with alkyl and/or hydroxyalkyl of up to 20 carbon atoms each. Typical of such N-heterocyclic radical are imidazolyl, N-alkylmorpholino, alkyl-

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pyrimidino, alkoxazolinyl, and the like. The substituents in formula I(c) are as follows:



wherein

Z is N or O;

o is an integer from 0 to 3;

p is an integer from 1 to 3

provided that the sum of o+p is from 3 to 4;

$R^1$  is defined as before and is linked to a ring carbon atom; and

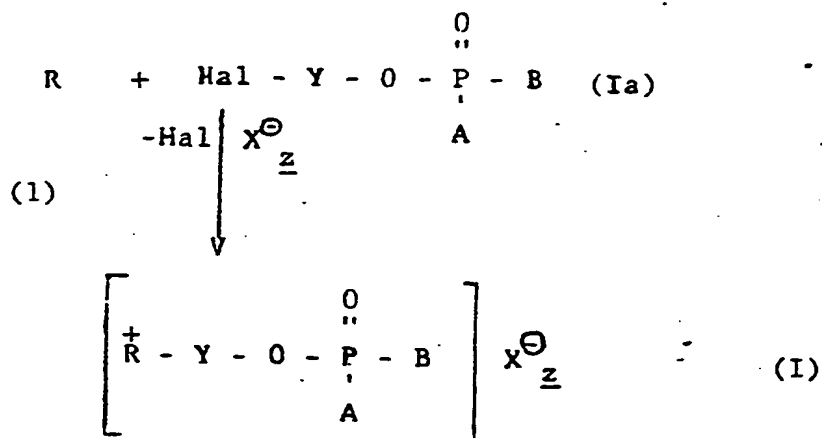
$R_6$  is, in the case of the tertiary amines (R), alkyl of from 2 to 6 carbon atoms which may be substituted with a hydroxyl group at the terminal or a non-terminal carbon atom, in the case of the secondary amines (R'),  $R_6$  is hydrogen.

The process of the invention is explained below with specific reference to the tertiary, secondary, and primary amine variants.

#### Tertiary Amine Reactants

When using a tertiary amine reactant for reaction with the phosphate-ester reactant, the process of the invention may be represented by the following generic reaction scheme (1):





wherein R is a tertiary amine, i.e., carrying three organic radicals, preferably containing a total of from 6 to 60 carbon atoms;

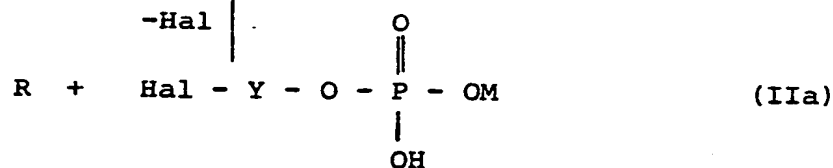
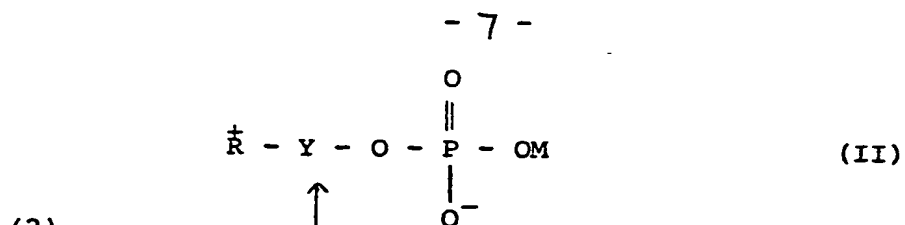
$\text{X}^{\ominus}$  is an anion; and

$\underline{z}$  is an integer from 0 to 2 and  $\underline{z}$  is of a value necessary for charge balance.

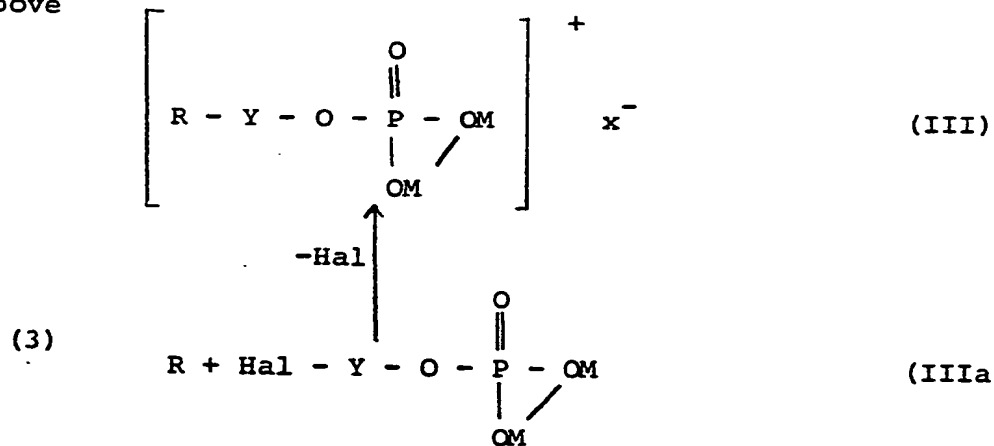
When both A and B in formula Ia is -O-Y-Hal, three moles of R are required per mole of phosphate reactant.

When B in formula I(a) is -O-Y-Hal, two moles of R are required per mole of phosphate ester reactant (Ia).

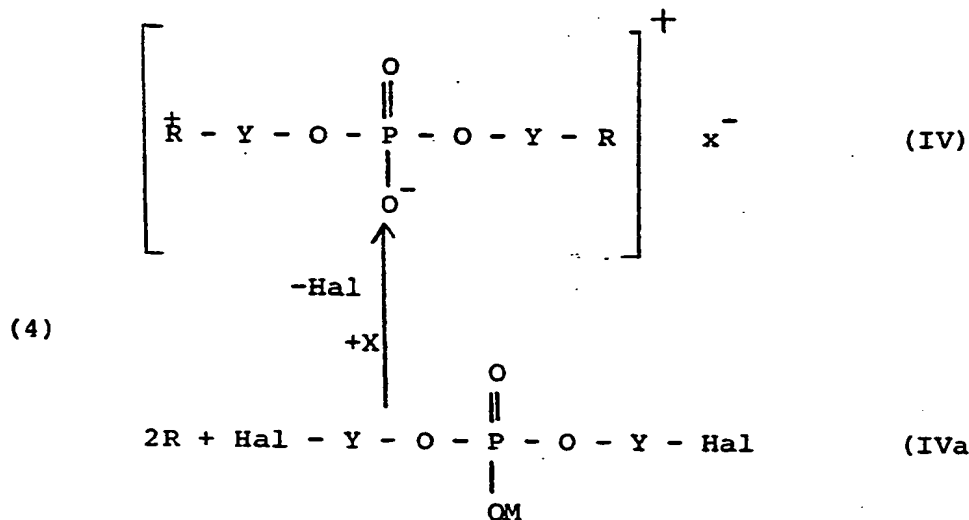
Still more specific sub-embodiments of reaction scheme (1), i.e., in which particular phosphate ester reactants are employed, can be represented as follows:



wherein Hal = halogen and the other radicals are defined as above



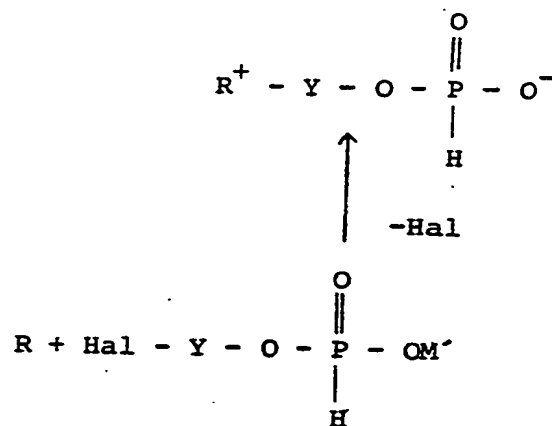
wherein the radicals are defined as above; and



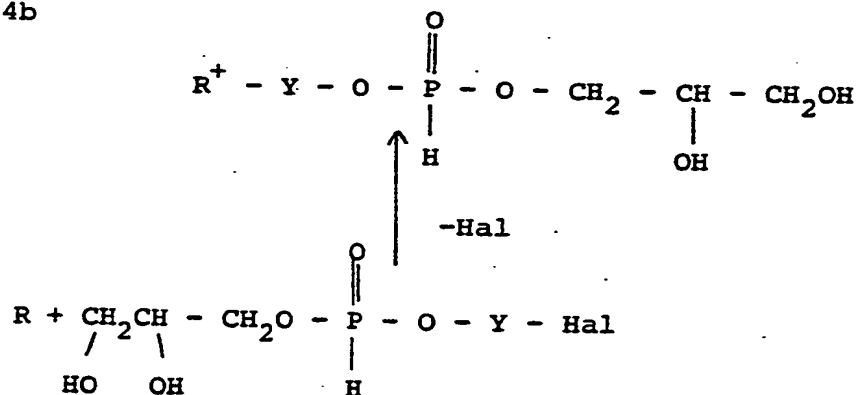
wherein the radicals are defined as above.

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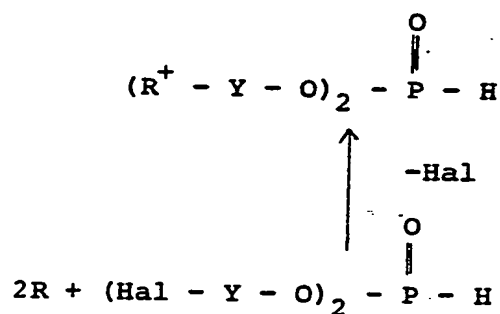
4a



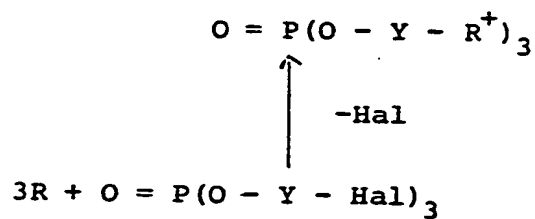
4b



4c



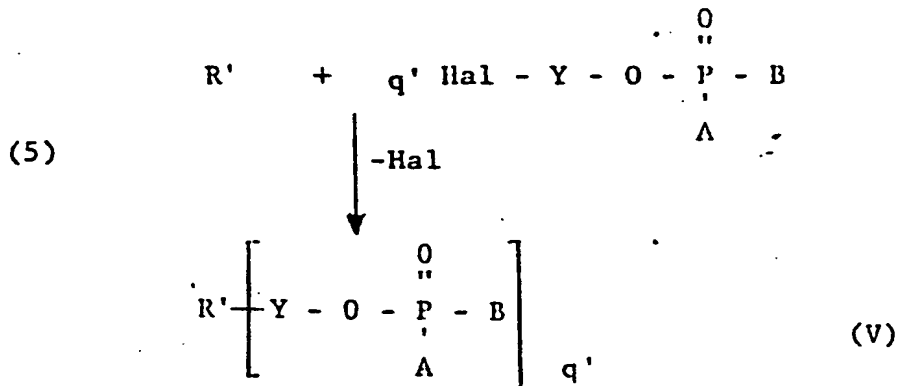
4d



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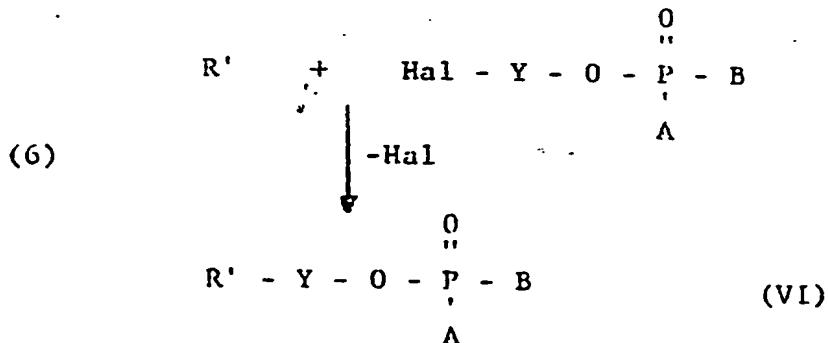
Secondary Amine Reactants

When using a secondary amine reactant with the phosphate-ester reactant, the process of the invention may be represented by the following generic reaction scheme:



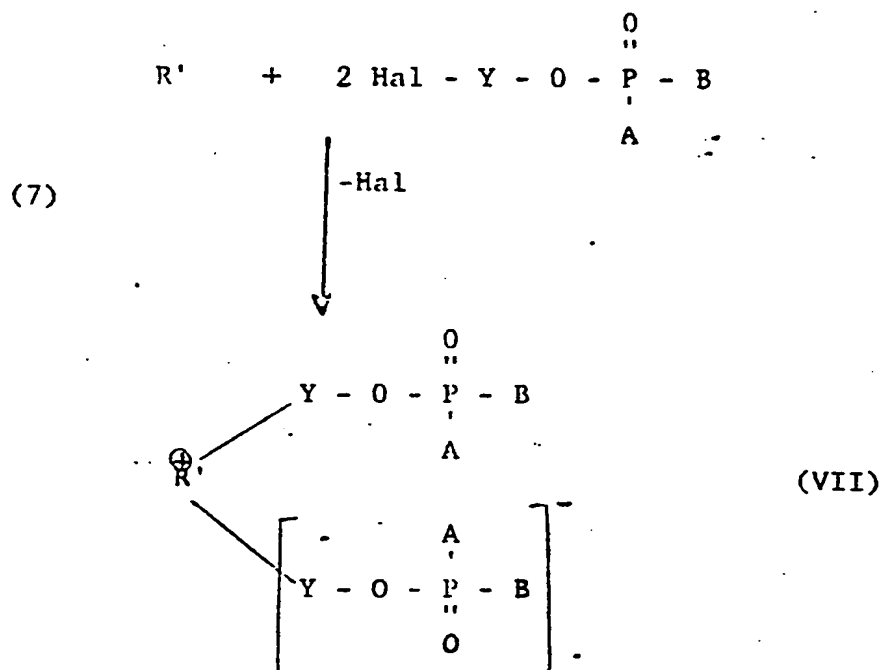
wherein R' is a secondary amine, i.e., carrying two organic radicals, preferably of a total of 6 to 60 carbon atoms, and q' is an integer from 1 to 2.

It will be understood that when one mole of phosphate ester reactant is employed per mole of secondary amine reactant R' (i.e., when q' = 1), the reaction proceeds as follows:



wherein the radicals are defined as above.

When two moles of the secondary amine reactant are supplied (i.e., when  $q' = 2$ ), the reaction leads to a bis-compound, as follows:



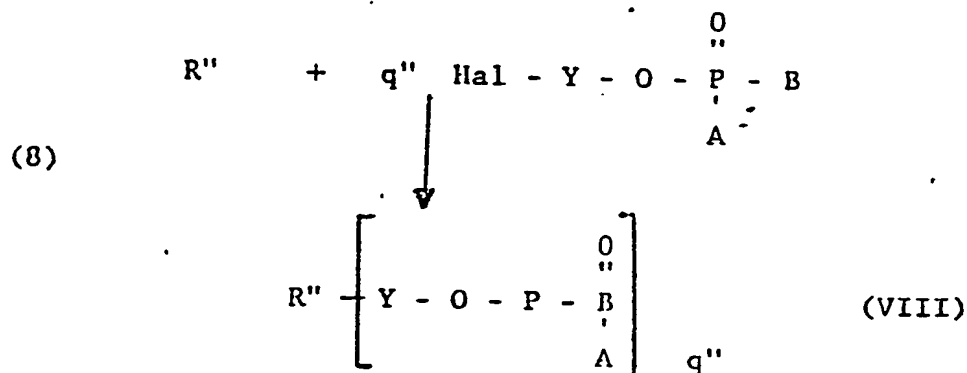
wherein the radicals are defined as above, and one of the A or B radicals is  $\text{O}^-$  as shown, for charge balance.

The secondary amine reactant  $\text{R}'$  can, in preferred and specific aspect, be of the formula I(b) given supra, provided, however, that  $\text{R}_3$  therein is hydrogen, to give the secondary amine function. Also,  $\text{R}'$  can be a cyclic amine reactant of the formula I(c) given supra, with the proviso that  $\text{R}_6$  therein is hydrogen, to give the secondary amine function.

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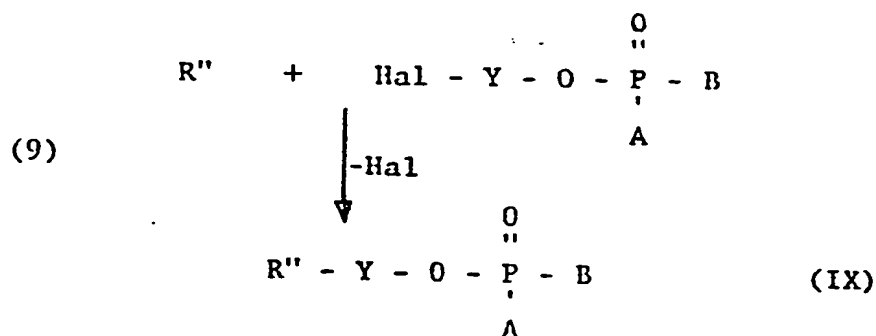
Primary Amine Reactants

When using a primary amine reactant with the phosphate ester reactant, the process of the invention may be represented by the following generic reaction scheme:



wherein R'' is a primary amine, i.e., carrying one organic radical, preferably of a total of 6 to 60 carbon atoms, and q'' is an integer from 1 to 3.

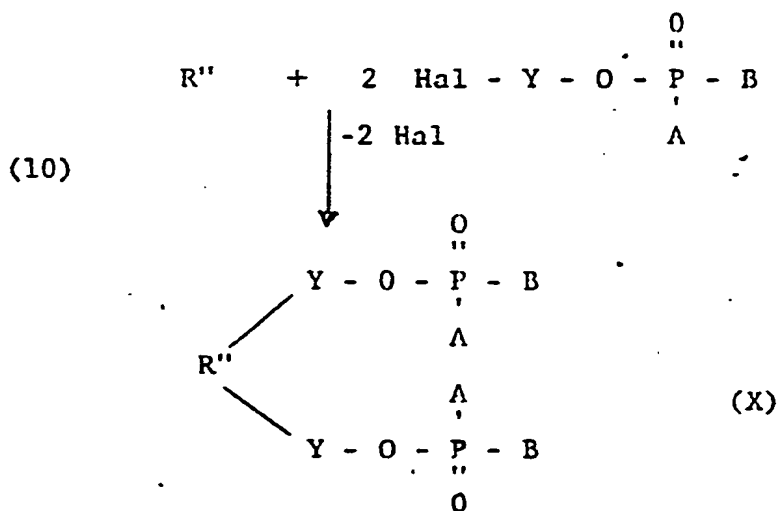
It will be understood that when one mole of phosphate ester reactant is employed per mole of primary amine reactant R'' (i.e., when q'' = 1), the reaction proceeds as follows:



wherein the radicals are defined as above.

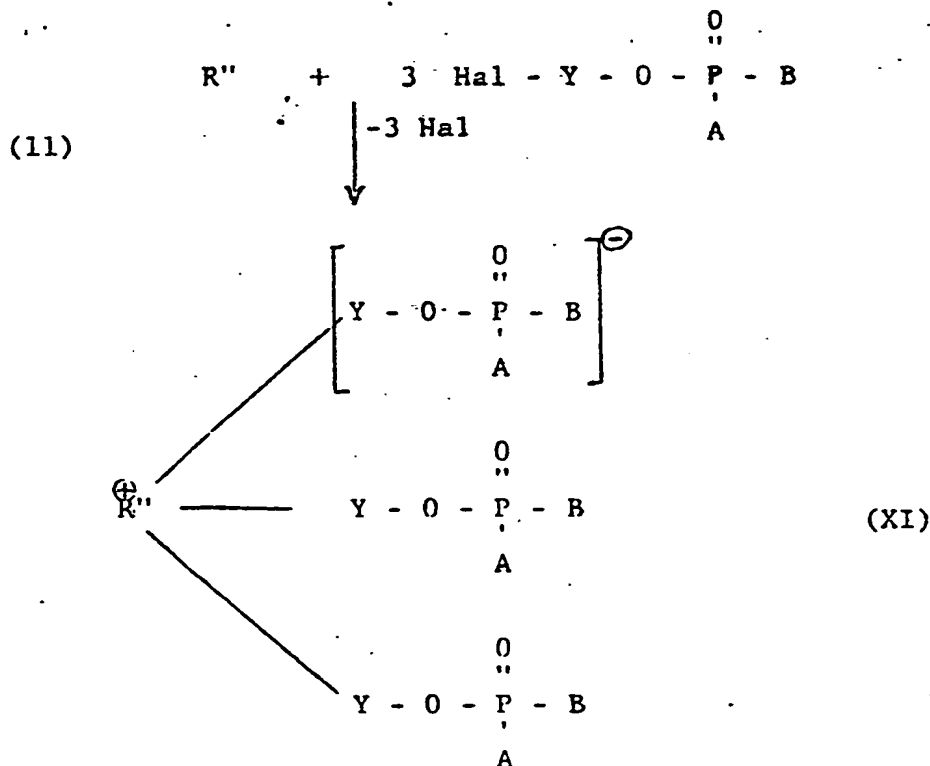
-12-

When two moles of the primary amine reactant are supplied per mol of phosphate ester reactant, i.e., when  $q''$  is 2, the reaction leads to a bis compound, as follows:



wherein the radicals are defined as before.

When three moles of the primary amine reactant are supplied, i.e., when  $q''$  is 3, the reaction leads to a tris- compound, as follows:

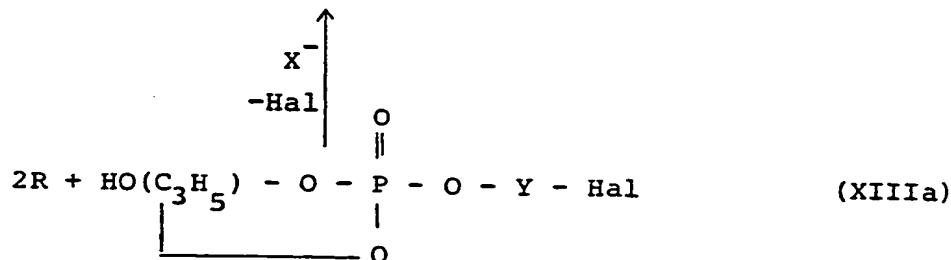
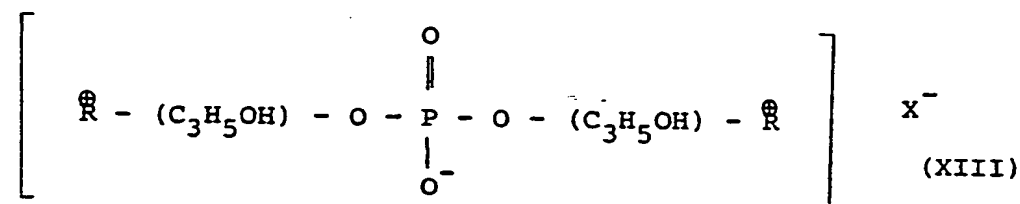
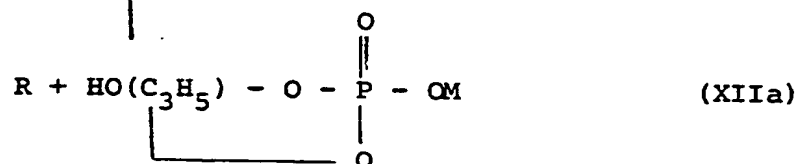
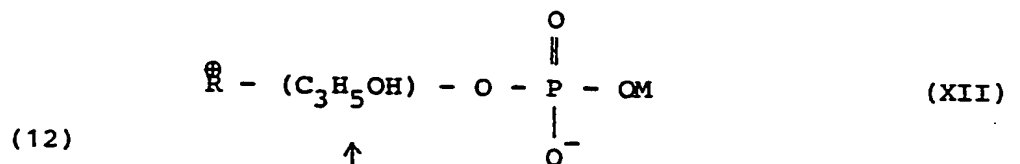


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wherein the radicals are defined as before, and one of the A or B radicals is  $O^-$  as shown, for charge balance.

The primary amine reactant  $R''$  can, in preferred and specific aspect, be of the formula I(b) given above, provided, however, that  $R_3$  and  $R_4$  therein are hydrogen, to give the primary amine function.

An alternative process for making certain of the surfactants utilizes a novel reaction between the amine reactant and a cyclic hydroxypropylene-containing phosphate ester reactant, to produce 3-hydroxypropylphosphobetaine, as shown schematically below for a tertiary amine reactant:





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wherein the reactants are defined as before, it being understood that the anion  $X^-$  can be supplied by the halide (Hal) group which is split from reactant IVa or VIa (in which case  $X^- = \text{Hal}$ ) or from another source, as explained above. The designations " $\text{HO}(\text{C}_3\text{H}_5)$ " or " $(\text{C}_3\text{H}_5\text{OH})$ " herein refer to a hydroxypropylene function in which the hydroxy can be linked to any one of the three carbons and the cyclic oxa- moiety is linked to one of the three carbons, either at the 3- or 2- position of the propyl group.

The reactions proceed in the same manner using primary amines ( $R''$ ) or secondary amines ( $R'$ ), instead of the tertiary amine ( $R$ ) shown, it being understood that use of secondary amines can give bis- compounds as in Reaction (7), supra, and use of primary amines can give bis- or tris- compounds, as shown in Reactions (10) and (11), supra, when the cyclic phosphate reactant is supplied in appropriate multiple molar ratio (2:1 or 3:1, respectively).

The reactants required in the processes can be prepared as follows:

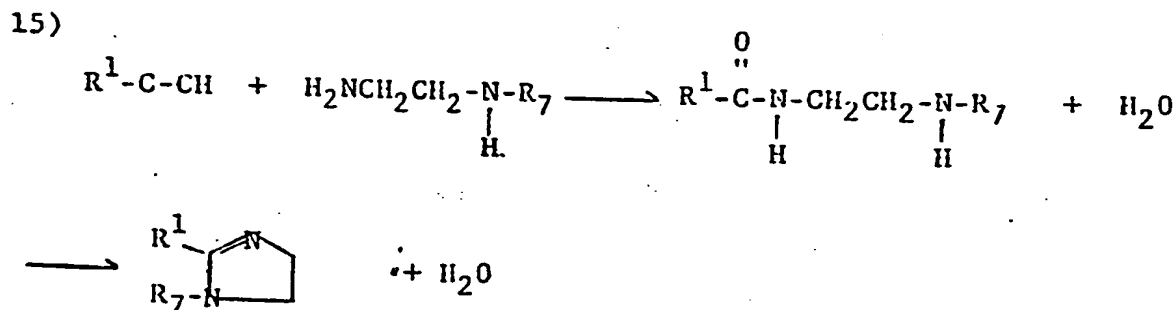
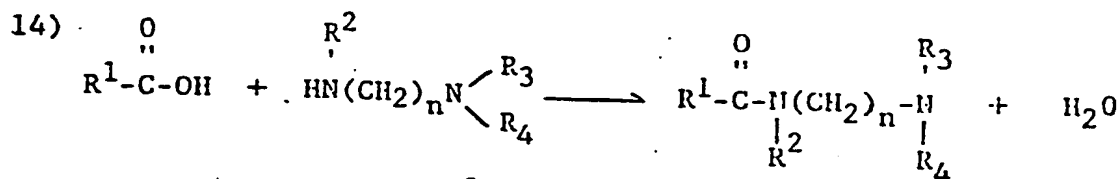
#### Preparation of Intermediate Amine Reactants

The amine reactants  $R$ ,  $R'$ , and  $R''$  are known or are generally prepared in accordance with conventional techniques. For instance, when making a tertiary amine ( $R$ ) of the amidoamine type (Ib), this can be prepared by reacting an acid with an aminoalkyl-substituted tertiary (or secondary or primary, in the case of  $R'$  and  $R''$ ) amine to result in the amidoamine function.

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Alternatively, an acid can be reacted with an aminoalkyl-substituted secondary or primary amine, followed by further treatment of the reaction product with alkylene oxide, to give the tertiary or secondary reactants, respectively. When R or R' is the N-heterocyclic structure (Ic), e.g., imidazolyl, this can be prepared in accordance with known techniques, e.g., as taught in U.S. Patent No. 2,267,965.

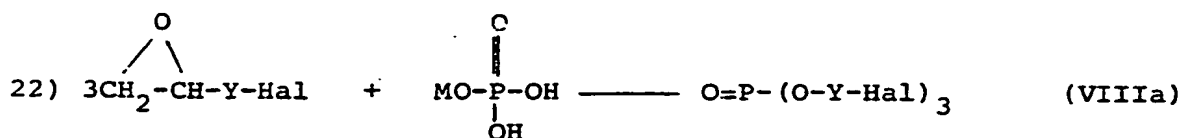
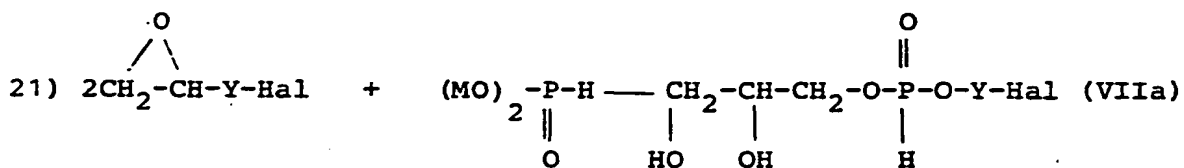
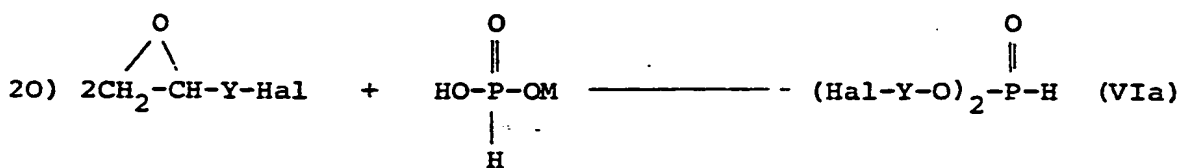
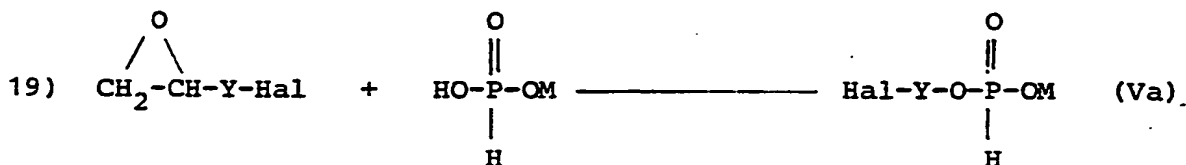
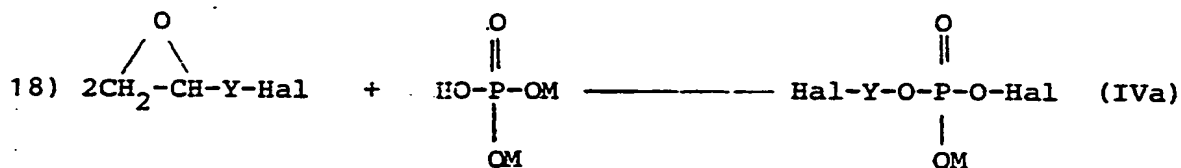
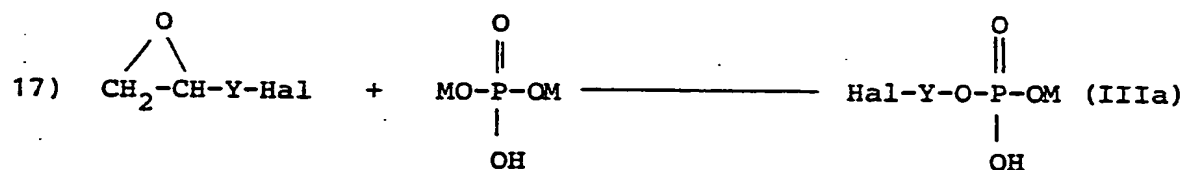
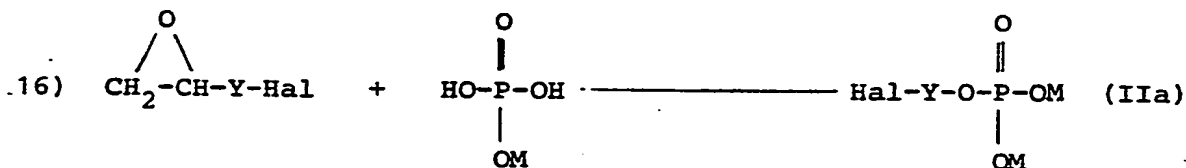
Reaction (14) below yields the non-cyclic reactants "R" and Reaction (15) illustrates the preparation of a typical cyclic amine reactant R (Imidazolyl):



wherein R<sup>1</sup> is defined as above and R<sup>7</sup> is alkyl of 2 to 6 carbon atoms which may be substituted with a hydroxyl group (at the terminal or a non-terminal carbon atom). This cyclic reactant can be prepared as disclosed in U.S. Patent No. 2,267,965.

Preparation of Phosphate Ester Intermediate Reactants

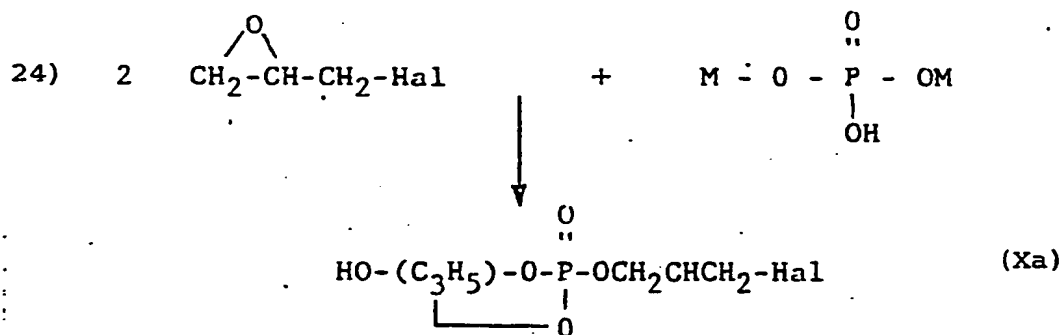
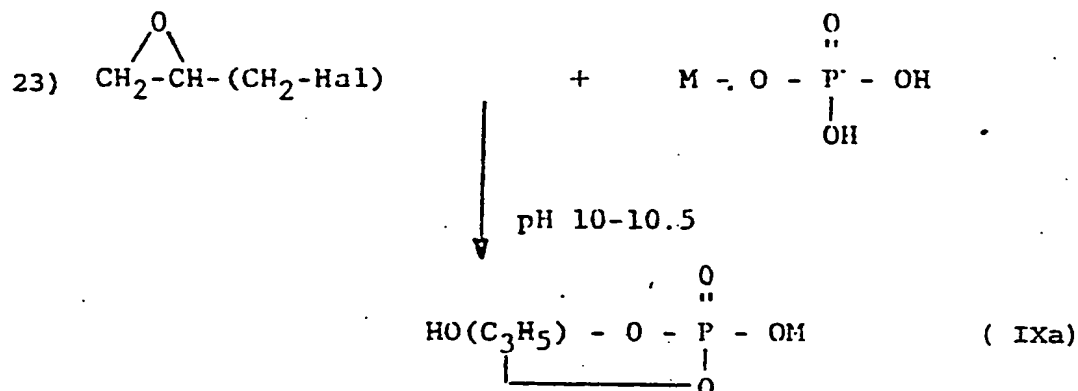
The preparation of the phosphate ester intermediate reactants I a through VIII a as set forth in the reaction sequences above are also prepared by reactions which are illustrated as follows:



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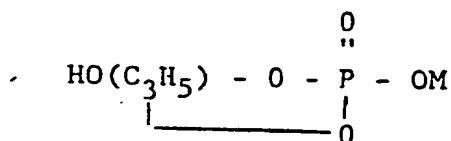
A wide variety of commercially available amines are suitable for these reactions. The amines can be primary, secondary or tertiary with only the proviso that the total number of carbons be greater than 6, i.e., to give a hydrophobe necessary for surface active properties. All other substitutions and modifications of the amine are usable in the present process. Of the commercially available aliphatic amines, there may be mentioned "Armeen" (Armak Chemical), e.g., octyl amine through dodecyl amine. Illustrative aliphatic secondary amines of similar molecular weight include such secondary amines as the "Armeen 2C" (dicocamine) through the disoya amine, tallow amine. Tertiary amines may be simple aliphatic tertiary amines such as the type alkyl dimethyl amine, dialkyl methyl amine, and trialkyl amine, marketed by Armak Chemical Company and an example is "Armeen DM14D". (which is the N-tetradecyl dimethyl amine). Further, ethoxylated aliphatic amines can also be used. These products are marketed under the names of "Ethameen". Any substitution is possible as illustrated elsewhere herein.

The cyclic phosphate ester intermediate reactants required for the alternative synthesis routes (12) and (13) supra, can be prepared as follows:

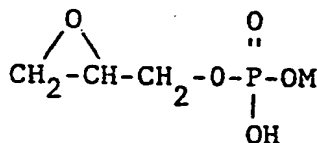


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It will be noted that Reactions 23 and 24 utilize reactants similar to the reactants needed in Reactions 17 and 18 supra (although with the more limited hydroxypropyl definition), but that different, cyclic, products are obtained. The different products are the result of a different pH adjustment; thus, while reaction 17) is carried out at a pH of about 4-5, reaction 18 is carried out at a pH of 9.5 to 10.5, resulting in a cyclic product. This cyclic product may contain also some vicinal epoxy material so that the formula



should be understood as including not only one or more of the isomers resulting from linkage of the oxa-oxygen to any one of the hydroxy-propylene carbons (to make a 5-, or 6-membered ring), but also the following structure:



Operation at a higher pH, e.g., 10.5 or higher, favors formation of the vicinal epoxy-containing material.

The reaction of epichlorohydrin with phosphoric acid and various phosphate salts has not been investigated to an appreciable extent and very little has been written in the literature on this reaction. We have observed that a variety of products can be obtained with variation of certain experimental parameters. The most important of these parameters include the pH of the phosphate salt, the mole ratio of the phosphate salt

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to the epichlorohydrin and the temperature at which the reaction is run. Reactions No. 16 through 18 occur in an acidic, aqueous solution. Consequently, the reaction proceeds by attack at the epoxide resulting in a 3-chloro-2-hydroxypropyl phosphate intermediate. This intermediate, containing a labile organic chlorine, is reacted with certain nucleophilic species, such as amine to give the product conforming to the general phosphobetaine structure. The pH at which this reaction occurs must be strictly controlled. The desired pH range is from 4 to 5. If the pH drops below 4 there is significant hydrolysis of the phosphate ester. If the pH at which the reaction is run is too high, there will be loss of labile organic chlorine. When the reaction is carried out in an alkaline environment of a pH 9.5 - 10.5 optimally, the resulting intermediate had surprisingly lost its labile organic chlorine and formed a cyclic diester. This diester is quite resistant to hydrolysis but extremely reactive towards certain nucleophilic species. This nucleophilic attack, particularly under conditions at which it is maximized, coupled with the proper selection of amine having a hydrophobic nature makes this process of the invention a commercially viable procedure for preparing surface active agents possessing unusual and valuable properties.

The following conditions represent preferred operating conditions:

- (1) The reaction should be carried out in an aqueous environment at a concentration of the reactants of 30-50% based on total solution (the balance being water); most preferably the reactants constitute about 40% of the total reactant/water mixture.

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- (2) The phosphate salt used should have the pH of 9.5 - 10.5 before the addition of epichlorohydrin. This will allow for maximum formation of the cyclic phosphate diester.
- (3) The reaction is preferably initially conducted at a temperature of 80 - 85°C under some pressure, e.g., 5 psig of nitrogen, to prevent azeotrope reflux. The temperature is gradually increased to 100°C and held until theoretical inorganic chloride is generated.

The reaction of epichlorohydrin with disodium and trisodium phosphate has been described or reported in the literature; O. Bailly, Compt. Rend. 172, 689-91 (1921); C.A. 15, 1884 (1921) and O. Bailly, Bull. Soc. Chim. (4) 31, 848-62 (1922); C.A. 17, 264 (1923). In the reported reaction of disodium hydrogen phosphates with epichlorohydrin a diglycerophosphoric acid diester was thought to have been obtained. As noted above, however we have found that the pH of this system has a profound effect on the product which is obtained. For example, by reacting  $\text{NaH}_2\text{PO}_4$  with epichlorohydrin, the following two products can be obtained, depending on the mole ratio of the two reactants.

If one mole of epichlorohydrin is reacted, the product is 3-chloro-2-hydroxypropyl phosphate (Intermediate Reactant A, below). If two moles are reacted, there is obtained bis(3-chloro-2-hydroxypropyl phosphate); Intermediate Reactant "D", below. These reactions are carried out at a pH of 4-5. Under these conditions, as can be seen from the products obtained, the phosphoric acid moiety attacks the epoxy ring. As the pH is



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increased to form disodium phosphate, a nucleophilic attack occurs with a displacement of significant quantities of chloride ions. This is shown in the appended drawing, in which

Fig. 1 is a plot showing the effect of pH on chloride generation.

At a pH of 9.5-10.5, theoretical chloride generation is achieved. Although it was assumed that simultaneous attack was occurring at the epoxy moiety, it was surprisingly discovered that the epoxide group was being retained essentially intact. The product obtained under these conditions was 2,3-epoxy-monosodium propyl phosphate (Intermediate Reactant "C", below). The presence of the epoxy group was subsequently verified by reaction with various amine compounds.

The various intermediates were used to react with various primary, secondary and tertiary amines to form the ultimate amphoteric phosphobetaine compounds. Although similar product would be expected to be obtained when utilizing Intermediate Reactants A and C, distinctly different properties were found for products prepared from these two intermediates. In the case of Intermediate Reactant C, significantly higher foaming products were obtained and this was later shown to be a function of pH of the initial phosphate salt used; this effect is depicted in the drawing wherein

Fig. 2 is a graph captioned "Foam Profile", which is a plot of foam height versus the pH of the initial phosphate salt used.

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One of the interesting phenomenon of these products is thus their pH dependent solubility. Not only are the products pH-dependent, but they are also concentration-dependent in that very dilute concentrations tend to become cloudy. The concentration at which this clouding phenomenon occurs is affected by the pH of the initial phosphate salt. This is shown in the appended drawing wherein

Fig. 3 is a plot of pH versus concentration at which cloudiness occurs.

At a pH of 9.5-10.5, there is a leveling off of the solubility.

As noted above, the process parameters must be controlled in order to maintain the reactive organic chlorine atom in the phosphate ester reactants and to avoid hydrolysis of these phosphate esters. Thus, the pH of the phosphate salt employed, the temperature of the reaction and the reaction time were all found to be important in yielding the desired intermediate product. The nature of the intermediate product in turn has a profound effect on the properties of the final products.

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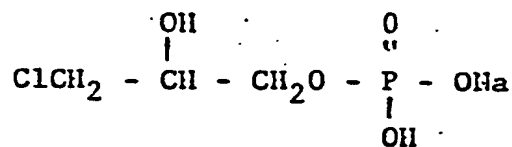
Indeed, the surprising reactivity of the cyclic phosphate ester intermediate reactants, like that of their labile chlorine containing analogues, while at the same time their stability against hydrolysis renders eminently suitable for use in the basic process of the invention to yield the ultimate surfactants.

When amine reactants are employed, which are sufficiently hydrophobic to surface-active, highly efficacious surface-active products are produced. However, non-surface-active analogues can also be prepared by using low molecular weight or hydrophilic amines.

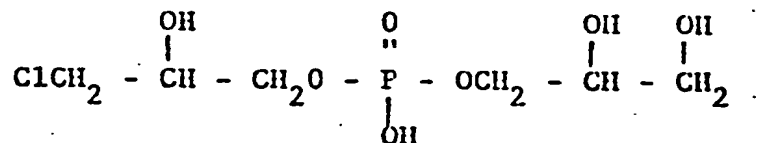
Specific phosphate ester intermediate reactants which were prepared according to reaction sequences 16-22 supra and which were used in the examples, infra, in conjunction with certain tertiary amine reactants, are set forth below:

Phosphate Ester Intermediate Reactants

Reactant "A" - Prepared According to Reaction Sequence

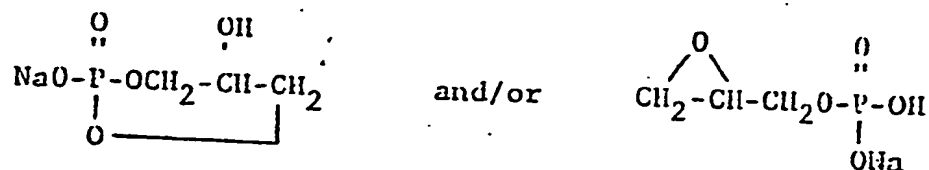


Reactant "B" - Prepared According to Reaction Sequence

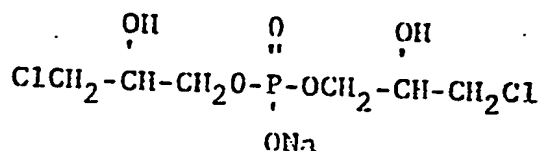


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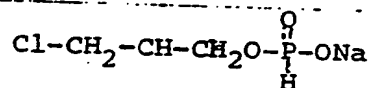
Reactant "C" - Prepared According to Reaction Sequence



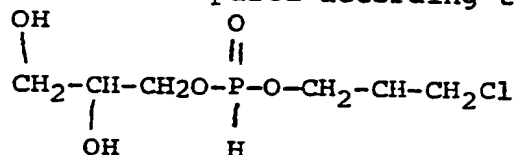
Reactant "D" - Prepared According to Reaction Sequence



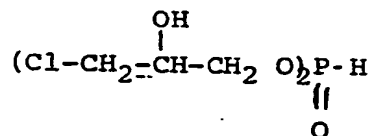
Reactant "E" Prepared according to Reaction Sequence



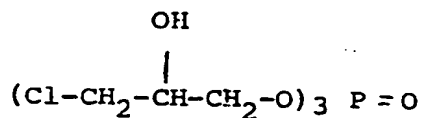
Reactant "F" Prepared according to the Reaction Sequence



Reactant "G" Prepared According to Reaction Sequence



Reactant "H" Prepared According to Reaction Sequence



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In carrying out the reactions 1 to 13 as set forth above leading to the ultimate compounds of the invention, the amine intermediate reactant (R, R', or R''), is reacted with the appropriate phosphate ester intermediate reactant and these reactions are generally carried out in an aqueous system at 80-100°C.

The optimum concentration range of the reactants in reactions 1 to 13 in aqueous solution is from 30-50% and most preferably the reactants constitute about 40% of the aqueous reactant mixture. In this respect, the preferred concentration are similar to those set forth above for certain intermediate reactions, e.g., in the preparation of the cyclic intermediates according to reactions 16 to 18 the resulting reactions product mixture, which preferably will contain about 40% of active reactants, may be used as such in carrying out the final reaction leading to the ultimate phosphorus-containing surface active products.

The phosphate ester reactant should have a pH of about 5 to 6 before the amine addition and the pH should be maintained at between 7 to 9 after said amine addition; below a pH of 7 the rate of quaternization slows significantly and, of course, the pH of the amines used themselves limit the pH on the alkaline topside at about pH 9.

As noted above, the reactions 1 to 13 are generally carried out at a temperature of about 80-100°C. The reaction is preferably initially conducted at a temperature of 80-100°C and may be conducted under some pressure, e.g., under 5 psig of nitrogen. However, under pressure, higher temperatures can be used, e.g., temperatures up to about 130°C and the ceiling temperature is determined by the sensitivity of the reactants, e.g., the amine reactant, since it will be found that color loss and evidence of

other degradation occurs at unduly high temperatures.

Many specific examples of ultimate phosphobetaine preparation are set forth below.

The ultimate reaction products are good surfactants and quite unexpectedly exhibit good foam volume and superior foam stability in comparison to commercially available amphoteric and zwitterionic surfactants. This was determined by an adaptation of the well known Ross-Miles foam test principle ["Oil and Soap" 18, 99-102 (1941)] in the following manner.

Lanolin, anhydrous, cosmetic grade is mixed with dioxane (technical grade) in the proportion of 2.5 grams lanolin and 100 grams of dioxane. The lanolin is first mixed with 25 cc of dioxane. This mixture is heated over a steam bath to 45°C in order to dissolve the lanolin in the dioxane. The remainder of the dioxane is then added and mixed. This lanolin-dioxane solution, which is stored in an amber bottle, should be prepared fresh on the day that the tests are run.

The composition to be tested is diluted by adding 376 cc of distilled water to 4 grams of the composition and then by adding 20 cc of the lanolin-dioxane solution described above while mixing. Heat is produced when the lanolin-dioxane solution is added to the solution of the composition in water and care must be taken in adjusting the temperature of this solution to 24-25°C. Both of these intermediate solutions should therefore be adjusted to 23°C before mixing. The cooling of the lanolin-dioxane solution should be gradual in order to avoid precipita-

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tion of the lanolin. This will produce a final solution with a temperature of 24-25°C.

The final solution of the composition to be tested, water, dioxane and lanolin described above, is then run in a modified Ross-Miles foam column in the usual way. All tests are conducted in duplicate, and the average of the two results is taken. Foam stability is determined by measuring the decay in foam height after two minutes, expressed as a percentage of the original height.

Typical foam values obtained utilizing the above procedure for an alkylamidophosphobetaine, an alkylamido betaine and an alkylamido sultaine are listed below:

	<u>Example No.</u>	<u>Foam Volume (ml)</u>	<u>% Decay After 2 min.</u>
Lauric Myristic Amido 3-Hydroxypropyl Phos- phobetaine	10	250	4.0
Cocamido Disodium 3-Hydroxypropyl Phos- phobetaine	9	240	10
Cocamido Disodium Ethyl Phosphobetaine	47	210	19
Cocamido Propyl- betaine	--	225	31.0
Cocamido Propyl- sultaine	--	200	60.0

As can be seen from the above results, the phosphobetaines made by the process of the invention exhibit excellent foam volume and stability, whereas the stability of the betaines and sultaines is significantly less.

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In another series of tests, additional species of the phosphobetaine compounds of the invention were tested by a "cylinder shake test" for the evaluation of foaming characteristics.

In this test, test solutions containing 0.1% by weight of the candidate surfactant in water of 100 ppm hardness (calcium to magnesium ration 3:2) were used and placed in 100 ml stoppered cylinders which had been cleaned so that water drains down its walls in an unbroken film. Each cylinder filled with test solution was shaken 20 times in a standard manner and net foam in ml is noted one minute and again five minutes after shaking. The test were run in three replicates. The results were as follows:



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<u>Lauric/Myristic Type</u>	<u>Example Number</u>	<u>1 Minute</u>	<u>5 Minutes</u>
Lauric Myristic Amido Betaine	--	67	60
Sodium Lauryl Sulfate	--	85	74
Lauric Myristic Amido Mono- sodium Phosphobetaine	2	88	78
Lauric Myristic Amido Disodium Phosphobetaine	10	85	78
Lauric Myristic Amido Glyceryl Phosphobetaine	2	86	78
Lauric Myristic Amido Carboxy Disodium Phosphobetaine	62	87	73
N-cocamidoethyl-N-hydroxy- ethyl glycine	--	76	67
<u>Coco Type</u>	<u>Example Number</u>	<u>1 Minute</u>	<u>5 Minutes</u>
Cocobetaine	--	65	56
Cocamidobetaine	--	70	63
Cocoamido Monosodium Phosphobetaine	1	79	74
Cocamido Glyceryl Phospho- betaine	20	71	74
Coco Imidazoyl Monosodium Phosphobetaine	37	83	78
Coco Imidazoyl Disodium Phosphobetaine	49	80	75
Bis(Coco Imidazoyl) Phospho- betaine	63	75	69

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In addition, the compounds of the present invention possess a surprisingly low ocular irritation potential when compared to commercially available amphoteric and zwitterionic surfactants. The test employed is the modified Draize Test (J.H. Draize et al, Toilet Goods Assn. Mo. 17, May, 1952, No. 1 Proc.Sci.Sect.).

In this method, a 0.1 ml sample of a neutral solution of the compound under investigation is dropped into one eye of an albino rabbit, the other eye serving as a control. Six rabbits are employed for each compound.

Observations are made after 1, 24, 48, 72 and 96 hours and 7 days after initial instillation; second and third instillations are made after the 24 and 48 hour readings. Results may vary from substantially no change, or only a slight irritation in the appearance of the rabbit's eye after 7 days, to severe irritation and/or complete corneal opacity. Ocular lesions are scored for the cornea, iris and conjunctiva with a higher number indicating greater ocular irritation and the scores are added to give a total numerical value for each reading for 6 rabbits and average. The averaged score is an indication of the irritation potential of the composition under test. Based on the averaged score, descriptive irritation evaluation may be given, e.g., none, slight, moderate, severe, etc.

Typical results for a betaine, sultaine and a phosphobetaine in accordance with the present invention when subjected to the above test procedure are as follows:

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<u>Compound</u>	<u>Eye Irritation Potential</u>						<u>Irritant Rating</u>
	<u>1 hr.</u>	<u>24 hr.</u>	<u>24 hr.</u>	<u>72 hr.</u>	<u>96 hr.</u>	<u>Day 7</u>	
Lauric Myristic Amido 3-Hydroxypropyl Phosphobetaine	7.7	0.3	1.3	1.0	0.0	---	slight
Cocamido Propylbetaine	11.7	4.2	9.3	13.2	11.2	5.8	severe
Cocamido Propylsultaine	15.0	8.5	15.6	25.0	----	---	severe

All tests were conducted at a concentration of 3% wt/wt.

In further series of tests carried out as above, but using only one test rabbit per compound, the following results were obtained:

	<u>Example Number</u>	<u>Day</u>					<u>Irritant Rating</u>
		<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>7</u>	
Lauric Myristic Disodium Amido Phosphobetaine	10	7	0	1	1	0	very slight
Glyceryl "CA-35"	33	4	0	0	0	0	very slight
Lauric Myristic Carboxy Disodium Phosphobetaine	62	2	2	0	0	0	very slight

#### Comparison

Amphoteric 20*	--	21	15	7	5	0	moderate
Lauric Myristic Amido Betaine	--	8	15	25	-	-	severe
Cocobetaine	--	23	26	19	17	25	severe
Cocamidobetaine	--	21	19	14	9	6	severe
Sodium Lauryl Sulfate	--	18	16	16	16	10	severe
CA-35**	--	26	21	21	16	0	severe

\* N-cocamidoethyl-N-hydroxyethyl glycine

\*\* 2-undecyl-1-hydroxyethyl propionic acid imidazoline

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As can be readily seen, the phosphobetaines in accordance with the present invention exhibit only slight ocular irritation, whereas the betaines and sultaines are severe irritants.

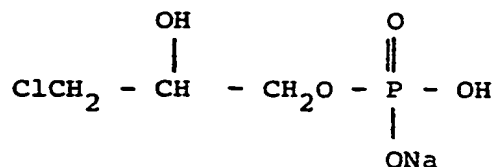
The following examples illustrate the processes of the invention and the novel intermediates utilized therein.

Example 1

## REACTANT "A"

60.00 parts of deionized water are charged into a suitable reactor to which 22.58 parts of  $\text{NaH}_2\text{PO}_4$  and 0.70 parts of NaOH are charged under good agitation. Mix well until a solution is obtained. 17.42 parts of Epichlorohydrin is charged under good agitation. The reactor is sealed and 5 PSIG  $\text{N}_2$  is applied. Heat to  $80-85^\circ\text{C}$ . holding the heated mixture at this temperature for 2 hours after the batch clears (approximately 3 hours total). Reaction is complete when theoretical reduction in acid value is obtained. Inorganic chloride will be less than 0.50%.

The product is an aqueous solution of a novel product having the following structure:



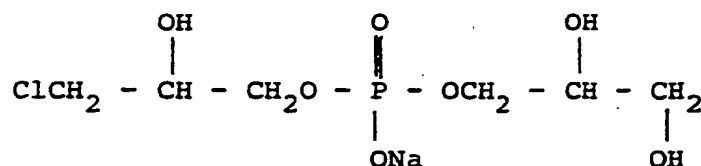
- 34 -

Example 2

## REACTANT "B"

60.00 parts of deionized water are charged into a suitable reactor to which 17.37 parts of  $\text{Na}_2\text{HPO}_4$  are charged. Mix well until a solution is obtained. 22.63 parts of Epichlorohydrin are charged under good agitation. The reactor is sealed and 5 PSIG  $\text{N}_2$  is applied. Heat to  $80-85^\circ\text{C}$ . holding the heated mixture at this temperature for approximately 2 hours after the batch clears (approximately 3 hours total). Reaction is complete when theoretical chloride is obtained and theoretical reduction in acid value is realized.

The product is an aqueous solution of a novel product having the following structure:

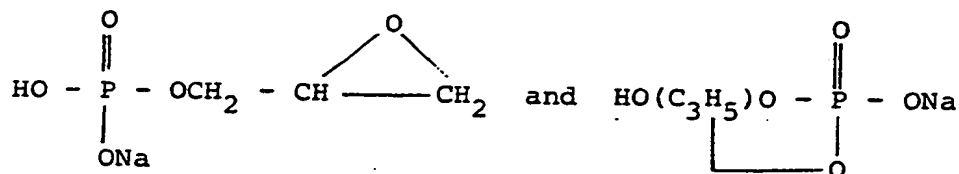
Example 3--

## REACTANT "C"

60.00 parts of deionized water are charged into a suitable reactor to which 24.22 parts of  $\text{Na}_2\text{HPO}_4$  are charged. Mix well until a solution is obtained. 15.78 parts of Epichlorohydrin are charged under good agitation. The reactor is sealed and 5 PSIG  $\text{N}_2$  is applied. Heat to  $80-85^\circ\text{C}$ . holding the heated mixture at this temperature for 2 hours after the batch clears (approximately 3 hours total). Reaction is complete when theoretical reduction in acid value and theoretical inorganic chloride values are obtained.

-35-

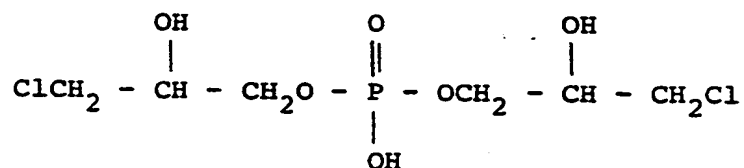
The product is an aqueous solution of a novel product having the following structure:

Example 4

## REACTANT "D"

60.000 parts of deionized water are charged into a suitable reactor to which 17.09 parts of  $\text{NaH}_2\text{PO}_4$  and 0.70 parts of  $\text{NaOH}$  are charged. Mix well until a solution is achieved. 22.91 parts of Epichlorohydrin is charged under good agitation. Reactor is sealed and 5 PSIG  $\text{N}_2$  is applied. Heat is applied to approximately  $80 - 85^\circ \text{C}$  and the heated mixture held at this temperature for approximately 3 hours after the batch clears (approximately 5 hours total). Reaction is complete when acid value is reduced by the theoretical amount. Inorganic chloride will be less than 0.5 %.

The product is an aqueous solution of a novel product having the following structure:

Example 5

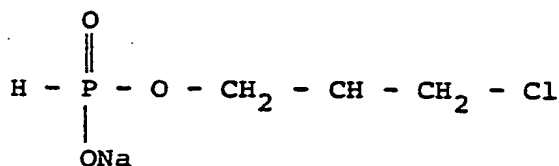
## REACTANT "E"

60.000 parts of deionized water are charged into a

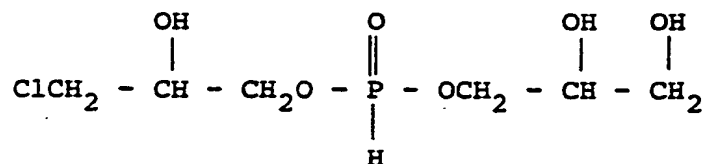
- 36 -

suitable reactor to which 21.17 parts of  $\text{NaH}_2\text{PO}_3$  is added. Mix well until solution is achieved. 18.83 parts of Epichlorohydrin is charged under good agitation. Reactor is sealed and 5 PSIG  $\text{N}_2$  is applied. Heat is applied to  $80 - 85^\circ \text{C}$ , and the reaction mixture is held at this temperature for approximately 3 hours after the batch clears (approx 5 hours total). Reaction is complete when acid value is reduced by theoretical amount.

The product is an aqueous solution of a novel product having the following structure:

Example 6

## REACTANT "F"

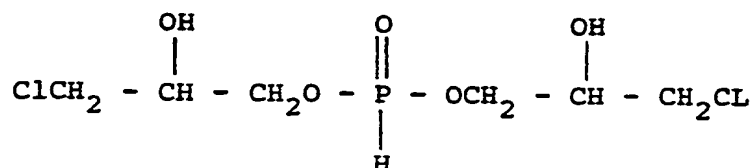


To 60.00 parts of soft water in a suitable reactor, slowly charge 16.20 parts of  $\text{Na}_2\text{HPO}_3$  under good agitation. Heat to  $40-50^\circ \text{C}$ . Slowly charge 23.79 parts epichlorohydrin under good agitation. Seal reactor and apply 5 PSIG nitrogen. Heat to  $90-95^\circ \text{C}$  and hold 3-4 hours. Reaction is complete when theoretical reduction in acid value has occurred and inorganic chloride reaches 50% of theoretical.

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Example 7

## REACTANT "G"



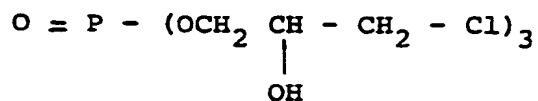
TO 60.000 parts of soft water in a suitable reactor, slowly charge 12.28 parts  $\text{NaH}_2\text{PO}_3$  under good agitation. Heat slowly to 40 - 45° C. Slowly charge 27.72 parts epichlorohydrin under good agitation. Seal reactor and apply 5 PSIG nitrogen. Heat to 90 - 95° C and hold 3 - 4 hours. Reaction is complete when there is no acid value.

Example 8

## REACTANT "H"

To 60.000 parts of water charge 21.1 parts of mono sodium phosphate in a suitable reaction vessel under good agitation. Apply heat to 50-55°C. Slowly charge 27.9 parts epichlorohydrin. Seal reactor and apply 5 psig  $\text{N}_2$ . Heat slowly to 80-85°C and hold 2 to 3 hours. Reaction is complete when acid value has been reduced to vanishingly small levels. Inorganic chloride levels will likewise be vanishingly small.

The product is an aqueous solution of a novel product having the following structure:



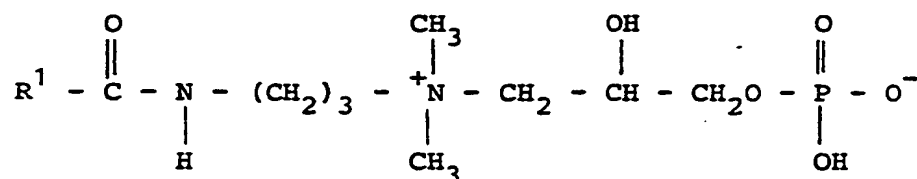


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Example 9

20.5 parts of Reactant "A" and 60.0 parts of water are charged in a reacting vessel under good agitation. Heat is applied to 50° C. 19.5 parts of molten 3-cocamidopropyl dimethylamine are slowly charged under good agitation. Heating is continued to 90 - 95° C and held at this temperature for 3 to 4 hours. Reaction reaches 97 % during this time via inorganic chloride and tertiary amine analysis.

The product is an aqueous solution of a novel product having the following structure:



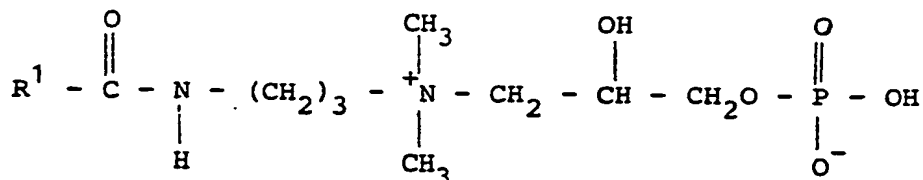
$\text{R}^1 = \text{C}_7 \text{ to } \text{C}_{17} \text{ alkyl}$

Example 10

20.8 parts of Reactant "A" and 60.0 parts of water are charged in a reacting vessel under good agitation. Heat is applied to approximately 50° C. 19.2 parts of a 70/30 blend of lauramido-propyl dimethylamine and myristamidopropyl dimethylamine are slowly charged to the above solution using good agitation. Heating is continued to 90 - 95° C and held at this temperature for 3 to 4 hours. Reaction reached 97 % during this time via inorganic chloride and tertiary amine analysis.

The product is an aqueous solution of a novel product having the following structure:

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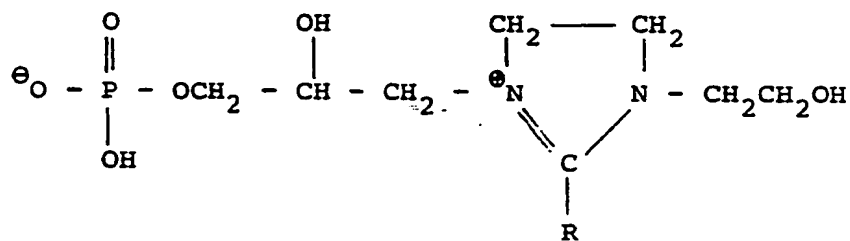
$R_1 = 70\% \text{ } C_{11} \text{ alkyl}$

$30\% \text{ } C_{13} \text{ alkyl}$

### Example 11

22.88 parts of Reactant "A" and 60.0 parts water are charged into a suitable reaction vessel under good agitation. Heat is applied to 50°C. 17.12 parts of 1-hydroxyethyl-2-alkyl-2-imidazoline (the alkyl has 7 + 17 carbon atoms) are charged under good agitation. Heating is continued to 90-95°C. and the heated mixture held at this temperature for 4 hours. Reaction reaches 97% during this time via inorganic chloride and tertiary amine analysis.

The product is an aqueous solution of a novel product having the following structure:



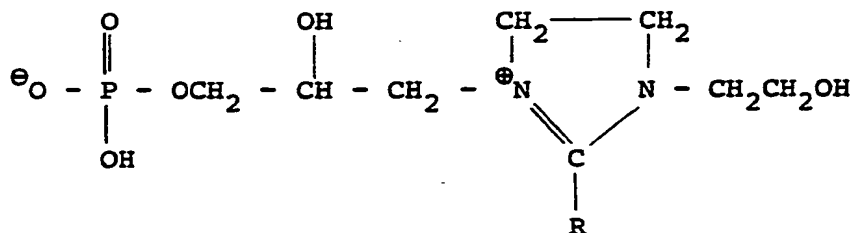
$R = C_7 \text{ to } C_{17} \text{ alkyl}$

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Example 12

20.8 parts of Reactant "A" and 60.0 parts of water are charged into a suitable reaction vessel under good agitation. Heat is applied to 50°C. 19.2 parts of 1-hydroxyethyl 2-alkyl-2-imidazoline (being C<sub>17</sub>) are charged under good agitation. Heating is continued to 90-95°C. and the heated mixture held at this temperature for 4 hours. Reaction reaches 97% during this time via inorganic chloride and tertiary amine analysis.

The product is an aqueous solution of a novel product having the following structure:



R = C<sub>17</sub> alkyl

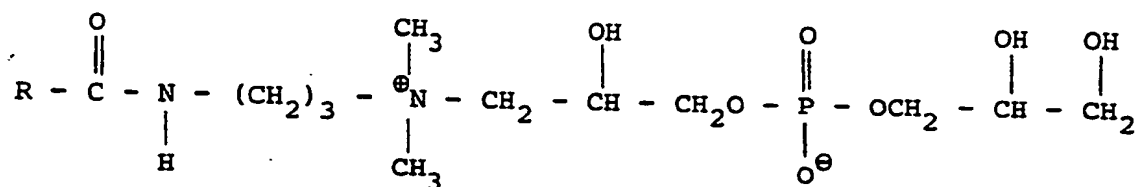
Example 13

26.8 parts of Reactant "B" and 60.0 parts of water are charged in a reacting vessel under good agitation. Heat is applied to approximately 50° C. 13.2 parts of 3-cocamidopropyl dimethylamine are slowly charged to the above solution using

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good agitation. Heating is continued to 90-95°C and the heated mixture held at this temperature for 3 to 4 hours. Reaction reaches 98% during this time via inorganic chloride and tertiary amine analysis.

The product is an aqueous solution of a novel product having the following structure:



R = C<sub>7</sub> - C<sub>17</sub> alkyl

#### Example 14

26.4 parts of Reactant "B" and 60.0 parts of water are charged in a reacting vessel under good agitation. Heat is applied to approximately 50°C. 13.6 parts of a 70/30 blend of 3-lauramidopropyl diethylamine and 3-myristamidopropyl diethylamine are slowly charged to the above solution using good agitation. Heating is continued to 90-95°C and the heated mixture held at this temperature for 3 to 4 hours. Reaction reaches 98% during this time via inorganic chloride and tertiary amine analysis.

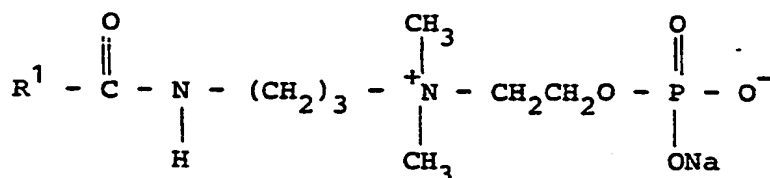
The product is an aqueous solution of a novel product having the following structure:

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Example 15

22.4 parts of Reactant "C" and 60.0 parts of water are charged in a reacting vessel under good agitation. Heat is applied to approximately 50° C. 17.6 parts of 3-cocamidopropyl dimethylamine are slowly charged to the above solution using good agitation. Heating is continued to 90 - 95° C and held at this temperature for 3 to 4 hours. Reaction reaches 97 % during this time via inorganic chloride and tertiary amine analysis.

The product is an aqueous solution of a novel product having the following structure:



$\text{R}^1 = \text{C}_7 - \text{C}_{17}$  alkyl

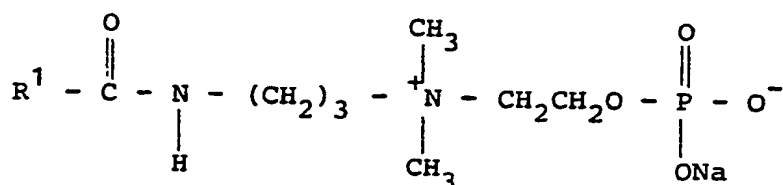
Example 16

25.7 parts of Reactant "C" and 60.0 parts of water are charged in a reacting vessel under good agitation. Heat is applied to approximately 50° C. 14.3 parts of a blend of 70/30 lauramidopropyl dimethylamine and myristamidopropyl dimethylamine are slowly charged to the above solution using good agitation. Heating is continued to 90 - 95° C and held at this temperature for 3 to 4 hours. Reaction reaches 97 % during this time via inorganic chloride and tertiary amine analysis.

The product is an aqueous solution of a novel product

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having the following structure:

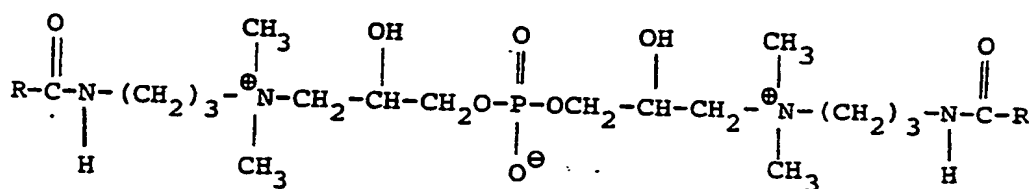


$\text{R}^1 = 70 \% \text{ C}_{11} \text{ alkyl}$   
 $30 \% \text{ C}_{13} \text{ alkyl}$

#### Example 17

14.4 parts of Reactant "D" and 60.0 parts of water are charged in a reacting vessel under good agitation. Heat is applied to 50°C. 25.6 parts of molten 3-cocamidopropyl dimethylamine are slowly charged under good agitation. Heating is continued to 90-95°C. and the heated mixture held at this temperature for 3 to 4 hours. Reaction reaches 98% during this time via inorganic chloride and tertiary amine analysis.

The product is an aqueous solution of a novel product having the following structure:



$\text{R} = \text{C}_7 - \text{C}_{17} \text{ alkyl}$

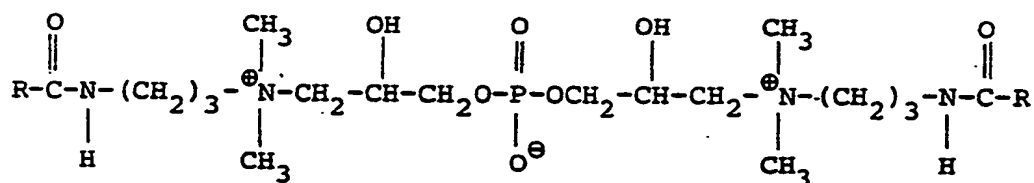
#### Example 18

15.3 parts of Reactant "D" and 60.0 parts of water are

- 44 -

charged in a reacting vessel under good agitation. Heat is applied to approximately 50° C. 24.7 parts of 70/30 blend of 3-lauramidopropyl dimethylamine and 3-myristamidopropyl dimethylamine are slowly charged to the above solution using good agitation. Heating is continued to 90 - 95° C and the heating mixture held at this temperature for 3 to 4 hours. Reaction reaches 98 % during this time via inorganic chloride and tertiary amine analysis.

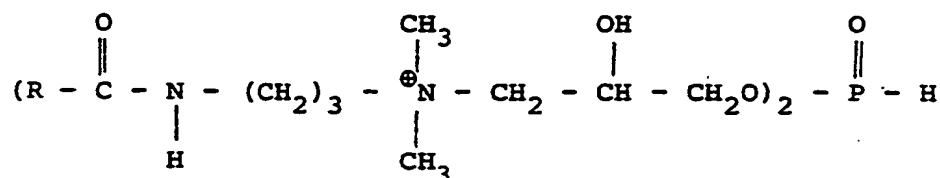
The product is an aqueous solution of a novel product having the following structure:



R = 70 % C<sub>11</sub> alkyl

30 % C<sub>13</sub> alkyl

#### Example 19



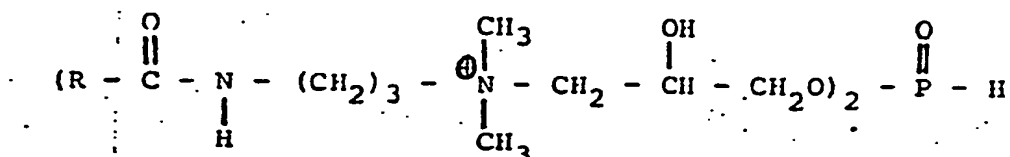
To 60.00 parts of soft water in a suitable reactor, charge 19.66 parts of Reactant "G" under good agitation. Heat to 45-50°C and charge 20.34 parts of 3 cocamido propyl dimethylamine under good agitation. Heat to 90-95°C and hold 4-5 hours. Reaction is complete when theoretical inorganic chloride is generated and when residual tertiary nitrogen levels become vanishingly small.

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The product is an aqueous solution of the above material.

R = C<sub>7</sub> - C<sub>17</sub>.

Example 20

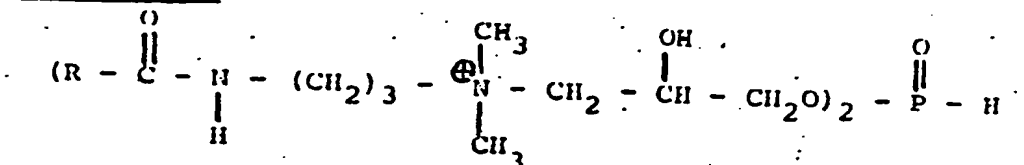


To 60.00 parts of soft water in a suitable reactor, charge 20.81 parts of Reactant "G" under good agitation. Heat to 45-50°C and charge 19.19 parts of 3 lauramido propyl dimethyl amine under good agitation. Heat to 90-95°C and hold 4-5 hours. Reaction is complete when theoretical inorganic chloride is generated and when residual tertiary nitrogen levels become vanishingly small.

The product is an aqueous solution of the above material.

R = C<sub>11</sub>

Example 21



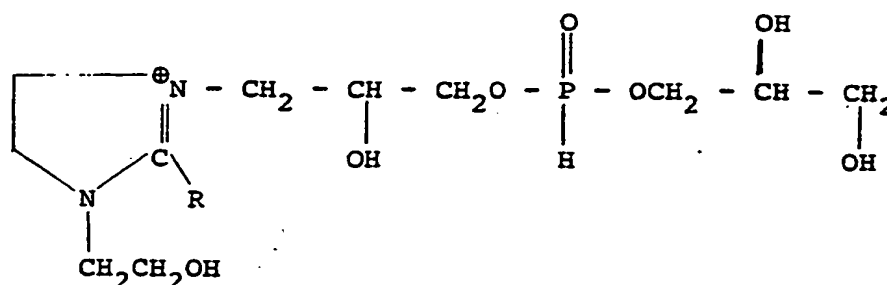
To 60.00 parts of soft water in a suitable reactor, charge 23.10 parts of Reactant "G" under good agitation. Heat to 45-50°C and charge 16.90 parts of 3 caprylamido propyl dimethyl amine under good agitation. Heat to 90-95°C and hold 4-5 hours. Reaction is complete when theoretical inorganic chloride is generated and when residual tertiary nitrogen levels become vanishingly small.

The product is an aqueous solution of the above material

R = C<sub>7</sub>



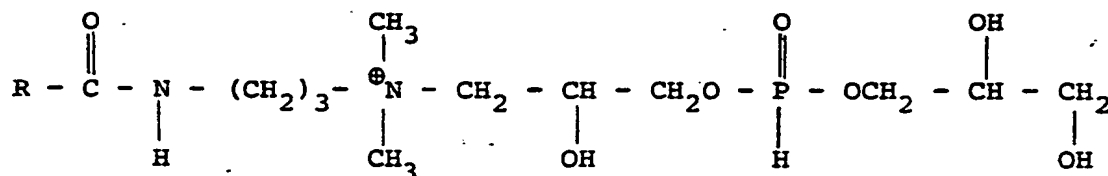
### Example 22



To 60.00 parts of soft water in a suitable reactor, charge 22.14 parts of Reactant "F" under good agitation. Heat to 45-50°C and charge 17.86 parts of 1 hydroxyethyl 2 alkyl 2 imidazoline (alkyl being C<sub>7</sub> to C<sub>17</sub>) under good agitation. Heat to 90-95°C and hold 4-5 hours. Reaction is complete when theoretical inorganic chloride is generated and when residual tertiary nitrogen levels become vanishingly small. The product is an aqueous solution of the above material.

R = C<sub>7</sub> - C<sub>17</sub>

### Example 23

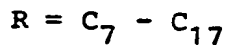


To 60.00 parts of soft water in a suitable reactor, charge 21.12 parts of Reactant "F" under good agitation. Heat to 45-50°C and charge 18.88 parts of 3 colamido propyl dimethyl amine under good agitation. Heat to 90-95°C and hold 4-5 hours. Reaction is complete when theoretical inorganic chloride is generated and when residual tertiary nitrogen

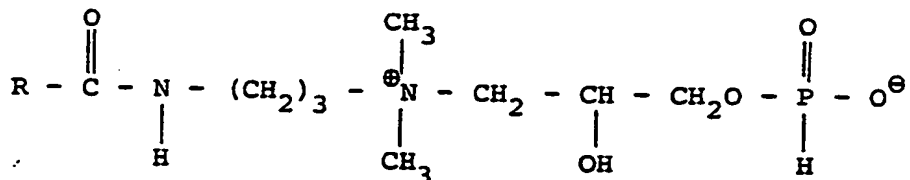
- 47 -

levels become vanishingly small.

The product is an aqueous solution of the above material

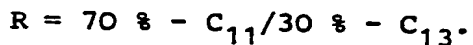


#### Example 24

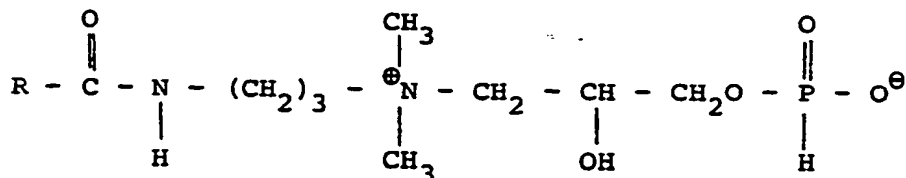


To 60.00 parts of soft water in a suitable reactor, charge 20.06 parts of Reactant "E" under good agitation. Heat to 40 - 45° C and charge 19.94 parts of a 70/30 blend of 3 lauramido propyl dimethyl amine + 3 myristamido propyl dimethyl amine under good agitation. Heat to 90 - 95° C and hold 4 - 5 hours. Reaction is complete when theoretical inorganic chloride is generated and when residual tertiary nitrogen levels become vanishingly small.

The product is an aqueous solution of the above material



#### Example 25



To 60.00 parts of soft water in a suitable reactor, charge 20.82 parts of Reactant "E" under good agitation. Heat to 45 - 50° C and charge 19.18 parts of 3 lauramido propyl dimethyl amine under good agitation. Heat to 90 - 95° C and hold 4 - 5 hours. Reaction is complete when theoretical inorganic chloride

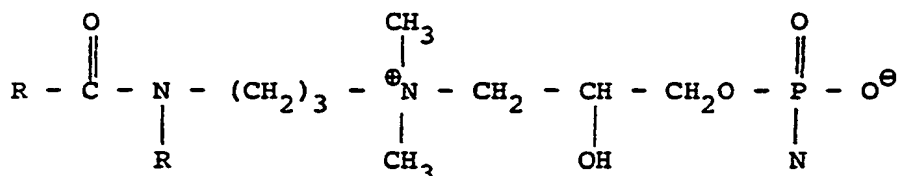
- 48 -

is generated and when residual tertiary nitrogen levels become vanishingly small.

The product is an aqueous solution of the above material.

R = C<sub>11</sub>

Example 26

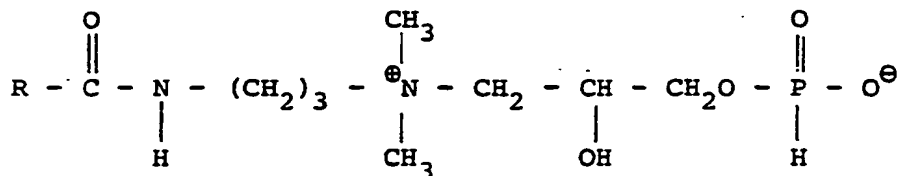


To 60.00 parts of soft water in a suitable reactor, charge 23.10 parts of Reactant "E" under good agitation. Heat to 45 - 50° C and charge 16.9 parts of 3 caprylamido propyl dimethyl amine under good agitation. Heat to 90 - 95° C and hold 4 - 5 hours. Reaction is complete when theoretical inorganic chloride is generated and when residual tertiary nitrogen levels become vanishingly small.

The product is an aqueous solution of the above material

R = C<sub>7</sub>

Example 27



To 60.00 parts of soft water in a suitable reactor, charge 24.45 parts of Reactant "E" under good agitation. Heat to 45 - 50° C and charge 15.55 parts of 3 caprylamido propyl dimethyl amine under good agitation. Heat to 90 - 95° C and hold 4 - 5 hours. Reaction is complete when theoretical inorganic chloride is generated and

- 49 -

when residual tertiary nitrogen levels become vanishingly small.

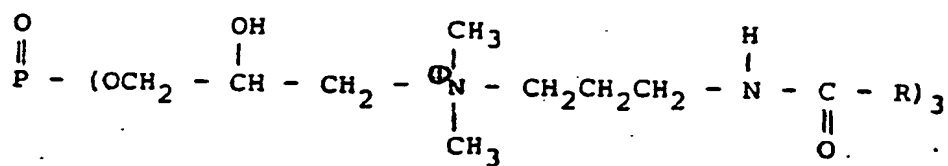
The product is an aqueous solution of the above material

$R = C_5$ .

#### Example 28

To 60.00 parts of soft water in a suitable reactor, charge 12.01 parts of Reactant "H" under good agitation. Heat to 45-50°C and slowly charge 27.99 parts of cocamidopropyl dimethyl amine under good agitation. Heat to 90-95°C and hold for 4-5 hours. Reaction is complete when inorganic chloride reaches theoretical and residual tertiary nitrogen levels are vanishingly small.

The product is an aqueous solution of the material shown below:



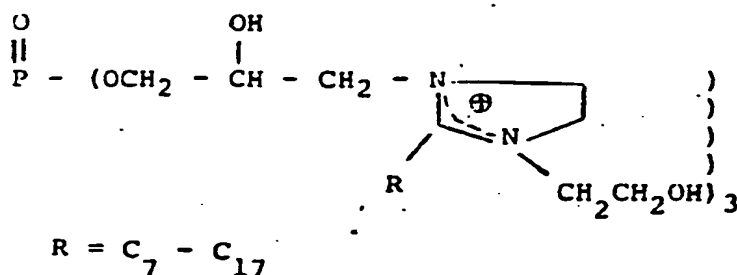
$R = C_7 \text{ to } C_{17}$

- 50 -

Example 29

To 60.00 parts of soft water in a suitable reactor, charge 12.17 parts of Reactant "H" under good agitation. Heat to 45-50°C and slowly charge 27.83 parts of 1-hydroxyethyl 2-alkyl imidazoline (alkyl being C<sub>7</sub> to C<sub>17</sub>) under good agitation. Heat to 90-95°C and hold for 4-5 hours. Reaction is complete when inorganic chloride reaches theoretical and residual tertiary nitrogen levels are vanishingly small.

The product is an aqueous solution of the material shown below:

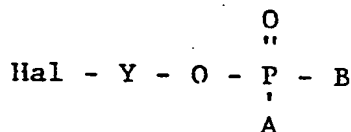


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WHAT IS CLAIMED

1. A process for the production of phosphorus-containing surface active agents, which process comprises reacting a phosphorus ester reactant selected from phosphate di- and tri-esters and phosphite di-esters, having either a labile halogen or a cyclic structure susceptible to nucleophilic attack, with an amine having at least 6 carbon atoms, to produce said surface active agent.

2. Process as claimed in claim 1 where said phosphorus-ester reactant is of the formula:



wherein

Hal is halogen

A is selected from OM, and OY Hal.

B is selected from H, OM', and OyHal

with the proviso that M' is an organic radical

Y may be alkylene, optionally interrupted by up to 2 oxygen atoms, of up to 12 carbon atoms, which alkylene chain may optionally be substituted with lower alkyl, alkoxy, hydroxy or hydroxyalkyl, e.g., of not more than 10 carbon atoms each;

M and M' are individually selected from the following:

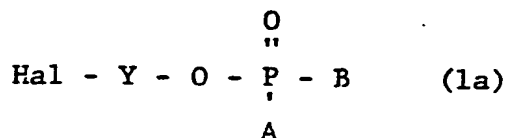
(a) hydrogen, (b) an organic radical selected from alkyl or hydroxyalkyl of up to 6 carbon atoms, polyhydroxyalkyl of up to 10 carbon atoms,

- 52 -

glyceryl, cycloalkyl of up to 6 carbon atoms, aryl or arylalkyl of up to 10 carbon atoms, or

(c) a salt radical selected from alkali metals (e.g., sodium or potassium), alkaline earth metals (e.g., magnesium or calcium), and mono-, di-, or triethanolamine.

3. Process as claimed in claim 2 wherein said phosphorus ester reactant is of the formula:



wherein

Hal is halogen

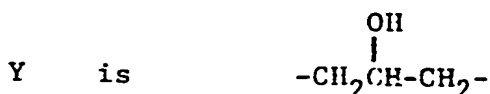
A is selected from OM, and OY Hal

B is selected from H, OM', and OYHal

with the proviso that M' is an organic radical

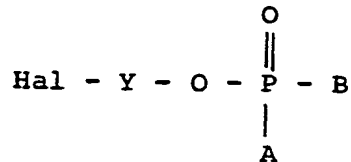
M and M' are individually selected from the following:

(a) hydrogen, (b) an organic radical selected from alkyl or hydroxyalkyl of up to 6 carbon atoms, polyhydroxyalkyl of up to 10 carbon atoms, glyceryl, cycloalkyl of up to 6 carbon atoms, aryl or arylalkyl of up to 10 carbon atoms, or (c) a salt radical selected from alkali metals (e.g., sodium or potassium), alkaline earth metals (e.g., magnesium or calcium), and mono-, di-, or triethanolamine; and



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4. Process as claimed in claim 3 wherein said phosphorus ester is of the formula:



wherein

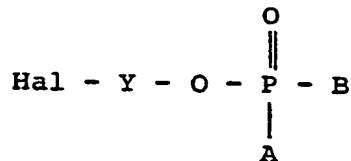
A is OM

B is OM'

M is Na

M' is Glyceryl

5. Process as claimed in claim 3 wherein said phosphorus ester reactant is of the formula:



wherein

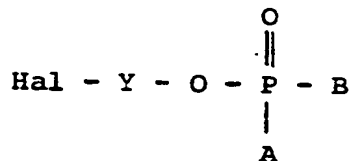
A is OM

B is OM'

M is Glyceryl

M' is  $\text{CH}_2\text{CHCH}_2\text{Cl}$   
 $\begin{array}{c} | \\ \text{OH} \end{array}$

6. Process as claimed in claim 3 wherein said phosphorus ester reactant is of the formula:



wherein;

A is OM

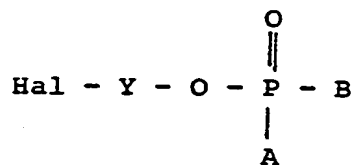
B is H

M' is Glyceryl



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7. Process as claimed in claim 3 wherein said phosphorus ester reactant is of the formula:



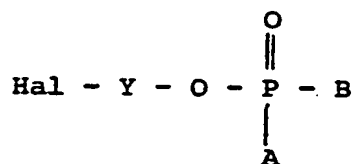
wherein

A is OM

B is H

M is  $\text{CH}_2\text{CHCH}_2\text{Cl}$   
 $\begin{array}{c} | \\ \text{OH} \end{array}$

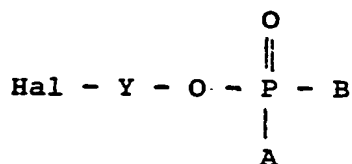
8. Process as claimed in claim 3 wherein said phosphorus ester reactant is of the formula:



wherein

Both A and B are  $\text{CH}_2\text{CHCH}_2\text{Cl}$   
 $\begin{array}{c} | \\ \text{OH} \end{array}$

9. Process as claimed in claim 3 wherein said phosphorus ester reactant is of the formula:



wherein

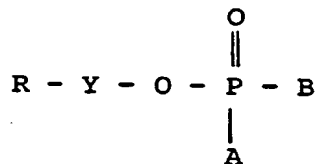
A is OM

B is OY Hal

M is Na

- 55 -

10. Phosphorus-containing surfactant agent having the structure



wherein

Hal is halogen

A is selected from OM, and OY Hal

B is selected from H, OM', and OY Hal

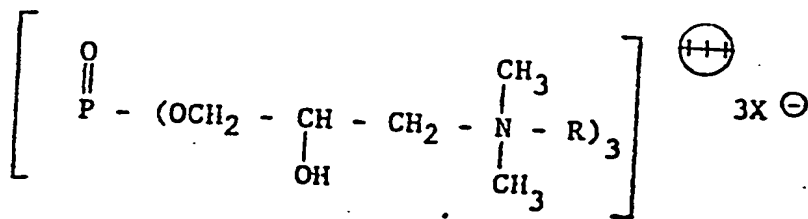
with the proviso that M' is an organic radical

Y may be alkylene, optionally interrupted by up to 3 oxygen atoms, of up to 12 carbon atoms, which alkylene chain may optionally be substituted with lower alkyl, alkoxy, hydroxy or hydroxyalkyl, e. g., of not more than 10 carbon atoms each;

R is a primary, secondary or tertiary amine having more than six carbon atoms.

M and M' are individually selected from the following: (a) hydrogen, (b) an organic radical selected from alkyl or hydroxyalkyl of up to 6 carbon atoms, polyhydroxyalkyl of up to 10 carbon atoms, glyceryl, cycloalkyl of up to 6 carbon atoms, aryl or arylalkyl of up to 10 carbon atoms, or (c) a salt radical selected from alkali metals (e. g., sodium or potassium), alkaline earth metals (e. g., magnesium or calcium), and mono-, di-, or triethanolamine.

11.) Phosphorus-containing surfactant as claimed in claim 1 having the structure:

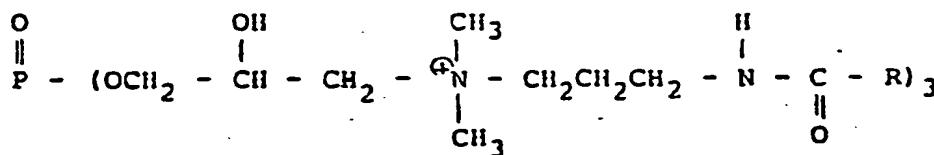


wherein

R is a tertiary amine radical of from 6 to 40 carbon atoms; and

X is an anion.

12.) Phosphorus-containing surfactant as claimed in claim 11 having the structure:

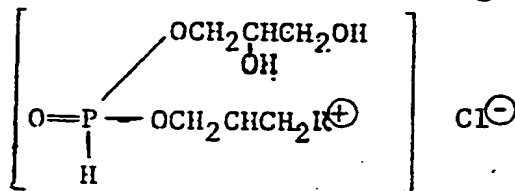


R = C<sub>7</sub> to C<sub>17</sub> alkyl

$$\begin{array}{ccccccc} \text{O} & & \text{OH} & & \text{O} & & \text{O} \\ \parallel & & | & & \parallel & & \parallel \\ \text{P} - & (\text{OCH}_2 - & \text{CH} - & \text{CH}_2 - & \text{CH}_2 - & \text{CO}^- & \text{C} - \text{R})_3 \\ & & & & | & & | \\ & & & & \text{CH}_2\text{CH}_2\text{OH} & & \text{H} \end{array}$$
$$\left[ \text{H} - \overset{\text{O}}{\underset{\text{OH}}{\text{P}}} (\text{OCH}_2\text{CH}(\text{CH}_2\text{R})_2)_2 \right]^+ 2\text{Cl}^-$$
$$\text{R}' - \underset{\text{O}}{\underset{\parallel}{\text{C}}} - \underset{\text{H}}{\underset{|}{\text{N}}} (\text{CH}_2)_3 \overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{N}^+}}$$

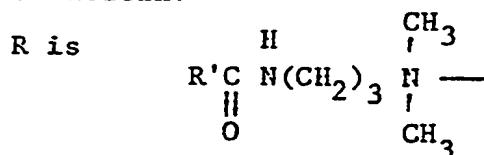
- 58 -

17. Phosphorus-containing surfactant of the formula



wherein R is a quaternary ammonium radical.

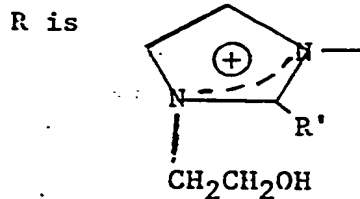
18. Phosphorus-containing surfactant as claimed in claim 17 wherein:



and

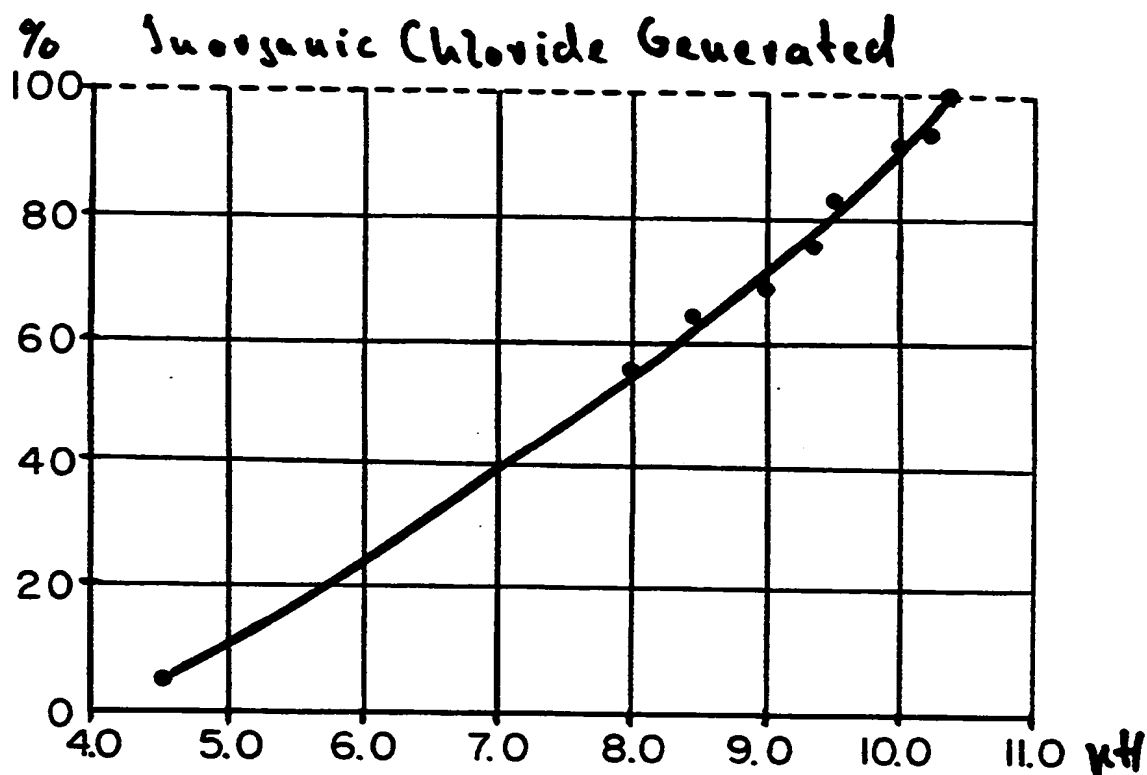
R' is C<sub>7</sub> to C<sub>17</sub> alkyl.

19. Phosphorus-containing surfactant as claimed in claim 17 wherein:



R' is C<sub>7</sub> to C<sub>17</sub> alkyl.

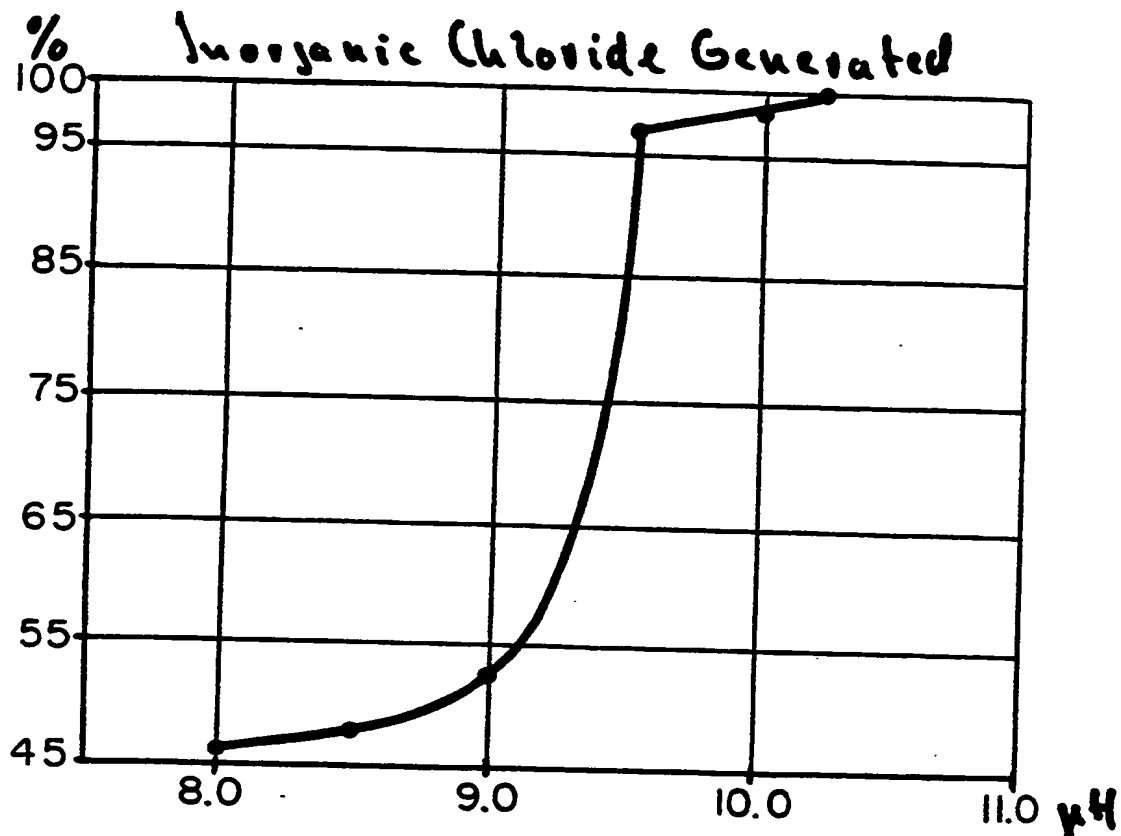
FIG. I.



pH	% Inorganic Chloride
4.6	5.5 %
8.0	54.0 %
8.5	63.0 %
9.0	66.2 %
9.4	75.0 %
9.5	83.6 %
10.0	91.0 %
10.2	95.0 %
10.3	100.0 %

-2/3-

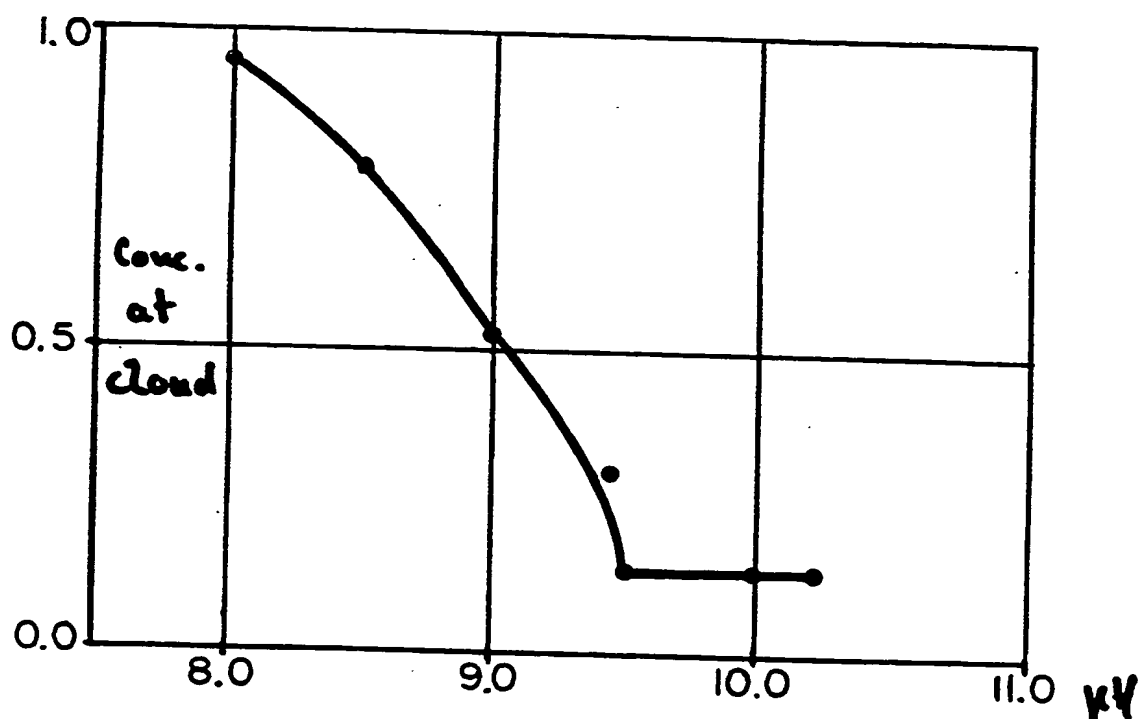
FIG. 2.



pH	% Inorganic Chloride
8.0	46
8.5	48
9.0	53
9.5	97
10.0	99
10.2	100

-3/3-

FIG. 3.



pH	Concentration at cloud
8.0	0.95 %
8.5	0.78 %
9.0	0.52 %
9.4	0.29 %
9.5	0.12 %
10.0	0.12 %
10.2	0.12 %



0013713



European Patent  
Office

# EUROPEAN SEARCH REPORT

Application number

EP 79 104 741.8

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl.)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
X	<u>US - A - 4 077 898 (ECONOMICS LABORATORY)</u> * claim 1, column 8, example 10 *	1	C 11 D 1/34 C 11 D 1/78 C 07 F 9/09
X	<u>US - A - 3 825 628 (KNAPSACK)</u> * claim 1 *	1	
A	<u>DE - A1 - 2 812 118 (COLGATE-PALMOLIVE)</u> * complete document * & FR - A1 - 2 385 839		
A	<u>DE - A - 2 260 326 (HOECHST)</u> * complete document *		<b>TECHNICAL FIELDS SEARCHED (Int. Cl.)</b>  B 01 F 17/00 C 07 F 9/00 C 11 D 1/00 C 11 D 3/00
P, A	<u>EP - A1 - 0 000 132 (VELSICOL CHEMICAL CORP.)</u> * complete document *		<b>CATEGORY OF CITED DOCUMENTS</b>  X: particularly relevant A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention E: conflicting application D: document cited in the application L: citation for other reasons
X The present search report has been drawn up for all claims			&: member of the same patent family, corresponding document
Place of search		Date of completion of the search	Examiner
Berlin		28-02-1980	SCHULTZE

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